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COAL-TAR AND AMMONIA

PART III—AMMONIA

COAL-TAR AND AMMONIA

DIRECTOR OF INDUSTRIES
Bengal

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APPENDIX

TABLES I., II., III.

FOR reducing the specific gravities of liquids lighter than water to the normal temperature of 15°·5 C.,=60° F.

Note.—The scale of reduction is not the same for high and low temperatures; hence three tables are given. When the observed temperature is *below* the normal, the figures in the table must be *deducted* from the observed specific gravity in order to reduce this to the normal temperature, and *vice versâ.*

I. For Specific Gravities of 0·880 downwards.

Degrees C. .	2	4	6	8	10	12	13½	15½
Deduct .	0·0105	0·009	0·008	0·006	0·0045	0·003	0·002	0

Degrees C. . .	17½	19½	21½	23	25	27	29
Add . . .	0·100	0·0025	0·004	0·0055	0·007	0·008	0·010

II. For Specific Gravities between 0·880 and 0·920.

Degrees C. .	2	4	5½	7	9	10½	12	14
Deduct	0·010	0·0085	0·0075	0·0065	0·005	0·004	0·001	0·00

Degrees C.	15½	17	19	20½	22	24	25½	27	29
Add . .	0	0·001	0·0025	0·0035	0·005	0·006	0·007	0·008	0·0095

III. For Specific Gravities between 0·920 and 0·960.

Degrees C.	1½	3	4½	6	7	8½	10	11½	13	14	15½
Deduct .	0·010	0·009	0·008	0·007	0·006	0·005	0·004	0·003	0·002	0·001	0

Degrees C	17	18	19½	21	22½	24	25	26½	28	29½
Add . .	0·001	0·002	0·003	0·004	0·005	0·006	0·007	0·008	0·009	0·010

TABLE IV.

For comparing the degrees of Baumé's, Cartier's, and Beck's Hydrometers with the corresponding Specific Gravities for liquids lighter than water.

Degrees.	Baumé.	Cartier.	Beck.	Degrees	Baumé.	Cartier.	Beck.
0	...	...	1·0000	17	0·952	0·955	0·9090
1	...	...	0·9941	18	0·946	0·948	0·9042
2	...	...	0·9883	19	0·940	0·941	0·8994
3	...	...	0·9826	20	0·933	0·934	0·8948
4	...	...	0·9770	21	0·927	0·928	0·8900
5	...	...	0·9714	22	0·921	0·921	0·8854
6	...	...	0·9659	23	0·915	0·914	0·8808
7	...	...	0·9604	24	0·909	0·908	0·8762
8	...	...	0·9550	25	0·903	0·901	0·8717
9	...	...	0·9497	26	0·898	0·895	0·8673
10	1·000	...	0·9444	27	0·892	0·889	0·8629
11	0·993	1·000	0·9392	28	0·886	0·883	0·8585
12	0·986	0·992	0·9340	29	0·881	0·877	0·8542
13	0·979	0·985	0·9289	30	0·875	0·871	0·8500
14	0·972	0·977	0·9239	31	0·870	0·865	0·8457
15	0·966	0·970	0·9189	32	0·864	0·859	0·8415
16	0·959	0·962	0·9139				

TABLE V.

For comparing the degrees of the Centigrade and Fahrenheit Thermometers.

C.	F.	C.	F.	C.	F.	C.	F.
+500	+932	+74	+165·2	+45	+113	+16	+60·8
400	752	73	163·4	44	111·2	15	59·0
300	572	72	161·6	43	109·4	14	57·2
200	392	71	159·8	42	107·6	13	55·4
100	212	70	158	41	105·8	12	53·6
99	210·2	69	156·2	40	104	11	51·8
98	208·4	68	154·4	39	102·2	10	50·0
97	206·6	67	152·6	38	100·4	9	48·2
96	204·8	66	150·8	37	98·6	8	46·4
95	203	65	149	36	96·8	7	44·6
94	201·2	64	147·2	35	95	6	42·8
93	199·4	63	145·4	34	93·2	5	41·0
92	197·6	62	143·6	33	91·4	4	39·2
91	195·8	61	141·8	32	89·6	3	37·4
90	194	60	140	31	87·8	2	35·6
89	192·2	59	138·2	30	86	1	33·8
88	190·4	58	136·4	29	84·2	0	32·0
87	188·6	57	134·6	28	82·4	- 1	30·2
86	186·8	56	132·8	27	80·6	2	28·4
85	185	55	131	26	78·8	3	26·6
84	183·2	54	129·2	25	77·0	4	24·8
83	181·4	53	127·4	24	75·2	5	23·0
82	179·6	52	125·6	23	73·4	6	21·2
81	177·8	51	123·8	22	71·6	7	19·4
80	176	50	122	21	69·8	8	17·6
79	174·2	49	120·2	20	68·0	9	15·8
78	172·4	48	118·4	19	66·2	10	14·0
77	170·6	47	116·6	18	64·4	11	12·2
76	168·8	46	114·8	17	62·6	12	10·4
75	167						

All the temperatures mentioned in this book are in Centigrade degrees, but can be converted into Fahrenheit degrees by means of the above table

ADDENDA

Comprising Patent Specifications and other New Matter published since the last Revise of the Proofs.

Page 13. *The treatment of Coal to obtain Oils, Ammonia, and other Products*, by subjecting it to the action of hydrogen or water-gas, at pressures above 100 atmospheres and temperatures between 300° and 500°, is described in the B. P. 18232, of 1914, of F. Bergius. It is asserted that under these conditions the hydrogen reacts with the coal, forming valuable hydrocarbons of low melting-points and ammonia, without producing uncondensable gases.

Page 54. *Production of Liquid Hydrocarbons from Coal.*—Jolicard (Fr. P. 475433) treats coal at 400° with nascent hydrogen, produced for example by introducing a mixture of superheated steam and air, or carbon monoxide. Catalyzers may be employed in the shape of chlorine or hydrochloric acid, or of copper, nickel, etc., deposited on the coal.

Page 60. *Tar-separators.*—The English patent of the Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft ("Bamag") for the invention described in the German patent 282276 is No. 16981, 1914.

Lelarge (B. P. 10394, 1914) filters the gases through a series of metallic spirals, coated with a viscous liquid; the axes of those of adjacent layers being at right angles.

Tschudy (U.S. P. 1155387) employs a distributing-chamber, and above this a separating-chamber, filled with checker work. The distributing-chamber has above the inlet pipe in its lower part a curved baffle-plate, fixed vertically in front, and above this a diaphragm with upwardly extended flanges, from which a tube descends into a central depression in the seal pot below.

H. T. Smith (B. P. 11246, of 1914) removes tar particles and other impurities from gas by passing the gas through a pervious medium, at sufficient velocity to cause the particles to be precipitated on the medium by the static electricity generated by the friction.

The Soc. d'Exploitation des Appareils Rateau (B. P. 13930, of 1914) describes a centrifugal fan for separating dust, tar, etc., from gases.

Page 61. *Removing the Tar from Coal-gas or Producer-gas, by a High-Tension alternating Electric Current.*—On this process, mentioned in the text, Hilgenstock (*Wasser und Gas*, 1915, p. 233) makes some communications. The electric current ionises the neutral tar particles, which causes them to reunite into coarser droplets, so that they can be collected in a mechanical tar-separator. The temperature has no influence on the ionising process. In this way the tar is so completely removed from the gas that naphthalene can be recovered from the gas-liquor in fine, white crystals. A further advantage is that, owing to the reduction of the surface of the tar particles, their absorbing action on benzene and toluene (which increases with the falling of the temperature) is lessened, and these hydrocarbons can therefore be more easily recovered from the gas (*cf.* p. 64). The process has also fully answered for removing the tar particles from producer-gas.

Page 62. *Production of Light Oils from Carbonaceous Substances.*—Rollason (B. P. 19697, of 1913) grinds coals, cannels, and shales, containing a high proportion of oxygen, mixes them with 3 to 5 per cent. of ground limestone or other suitable carbonate, and heats the mixture slowly in retorts, to about 500°. The carbon dioxide given off from the limestone tends to prevent the combination of oxygen and hydrogen, and favours the production of oils. The same (B. P. 18490, 1914) produces light oils of sp. gr. 0·90 to 0·98 from coal, cannel, coal shale, and crude oils, by adding 4 to 6 per cent. limestone to the material, the amount depending on the density of oil required. The mixture is distilled at 175° to 400°. The furnace setting has a large heat capacity, so that the charge is heated during the period when water-vapour and hydrocarbons are formed. The water-vapour prevents the decomposition of the hydrocarbons while in the retort.

Page 70. *Recovery of Benzene from Illuminating-gas.*—Herring (*J. Gas Lighting*, 1915, p. 569) states the yields obtained with a revolving washer. The illuminating-value of the gas is considerably diminished by the extraction of the benzene, but its heating-value is not greatly affected.

According to *Gas World* (quoted in *Chem. Trade J.*, 1916, p. 166), the Italian Government have made regulations for the compulsory washing of all coal-gas, to extract benzol, soluol, and xylol for military and other purposes, leaving in the gas enough of those hydrocarbons so as not to reduce the heating-value below 517 B.T.U. per cubic foot, or the lighting-value to less than two-thirds.

Hirzel (Ger. P. 290119) describes an apparatus for the complete recovery of benzol and its homologues and of naphthalene from coke-oven gases.

Page 81. *Recovery of Toluene from Coal-gas.*—According to *Chem. Trade J.* 1915, vol. lvii., p. 181, the Oldham Corporation are treating the whole of the town's gas for toluene, but complaints were made of the poor quality of the gas now supplied to the customers, and it was found that the extraction of the toluene certainly robbed the gas of some of its illuminating power.

According to Rollason (*J. Gas Lighting*, 1915, cxxxi., p. 696), the toluene content of the gas can be raised by washing them, after cooling, with the tar made during carbonization. This increase depends on the age of the coal used; its oxygen content, and on the temperature of carbonization. Second-grade and semi-coking coals give off their hydrocarbons very quickly; where high temperatures are employed, the hydrocarbons are decomposed into methane and hydrogen, and the coke remaining behind is soft and friable. When adding limestone and then carbonizing at a temperature above 850°, the quality of the gas is improved, the quality both of gas and of ammonia is increased, and the sulphur content of the gas is reduced. With a coal carbonized at 1008° to 1210°, the toluene recovered on washing with anthracene oil rose from 2·96 lb. per ton of coal without limestone, to 3·8 lb. with limestone, and the amount of toluene recovered from the tar rose from 0·14 lb. to 0·41 lb. At a lower temperature of carbonization the increase of toluene was even greater.

The recovery of toluene from illuminating-gas is discussed by an "expert" in *J. Gas Lighting*, cxxxi., pp. 635 *et seq.* (1915).

Page 87. *Determination of Benzol in Gas.*—Neubeck (*J. Gasbeleucht.*, 1915, lviii., p. 616; *J. Gas Lighting*, 1915, cxxxii., p. 264) found the method of absorbing the benzol in washing-oil and distilling the resulting solution up to 120° unreliable. He passes a measured volume of gas, dried by calcium chloride, into a cooling-coil, having a small bottle containing paraffin oil at its lower end, and immersed in a freezing-mixture of solid carbon dioxide and ether contained in a Dewar vacuum vessel, whereby a temperature of −78° is attained. The paraffin oil absorbs any benzene vapour given off during the manipulation. The increase in the weight of the apparatus, including the paraffin oil, on being removed from the freezing-mixture and allowed to attain the normal temperature, indicates the benzol contained in the volume of gas used; the benzol can be afterwards tested by distillation. The results obtained by this method from a known quantity of benzol volatized into air, proved its accuracy.

Reineke (Ger. P. 285920) estimates the benzol in coal-gas by measuring the illuminating power of the gas by means of a photo-electric cell, *e.g.* a selenium cell.

Graul (U.S. P. 1163654) makes a continuous test of the gas as produced by removing the naphthalene from a sample by treatment with picric acid, dividing the remaining gas into two parts, removing the benzene from one of them, *e.g.*, by absorption oil, and then burning the two parts separately and comparing the illuminating value of the flames.

Page 95. *Statistics on Coke-ovens fitted with Recuperation Plant.*—In *Great Britain*, according to Bone (quoted in *Chem. Ind.*, 1916, p. 50) the quantity of coal carbonized in ovens provided with recuperative plants has been:—

Year.	
1898	1·25 million tons
1905	3·3 "
1907	7·5 "
1913	13·5 "

The quantity of coal carbonized in the old-style beehive ovens in 1913 was only 6·5 million tons.

In *Russia* (according to *Chem. Trade J.*, 1916, vol. lviii., p. 101) the number of coke-ovens fitted with recuperation plant in 1914 was 1208, and further 486 ovens were under construction.

Page 95. *Statistics on the Recovery of Tar and Ammonia from Coke-ovens in the United States.*—According to the United States Geological Survey (quoted from *Chem. Trade J.*, 1915, lvii., p. 477), during the year 1914, 192 new retort ovens were constructed in the United States, against 587 beehive ovens. The total number of retort ovens in 1914 showed an increase of 121, that of beehive ovens a decrease of 3016. Of the former, 667, of the latter, 44,450, were idle during 1914. At the close of 1914, 644 new retort ovens and 605 beehive ovens were in course of construction. The quantities of products obtained from by-product ovens were:—

Year.		1913.	1914.
Gas	*M cubic feet*	64,553,941	61,364,375
Tar	*gall.*	115,145,025	109,981,315
Ammonia, sulphate, or reduced to equivalent of sulphate	*lb.*	173,342,349	170,763,906
Ammonia liquor	*gall.*	4,102,448	5,938,233
Anhydrous ammonia (mainly ammoniacal liquor sold on pound basis of NH_3)	*lb.*	28,663,936	25,370,509
Other by-products (mainly benzol)	*value*	$403,579	$997,007
Coke	*short tons*	12,714,700	11,219,943

According to Lesher (quoted in *Z. angew. Chem.*, 1916, iii., p. 148) there was obtained in the United States in 1915 from by-product coke-ovens: 13,942,763 gall. benzol and other light oils, and 761,256 lb. naphthalene.

According to *Chem. Trade J.*, 1916, p. 195, the United States Steel Corporation was going to build 1500 by-product coke-ovens, at a cost of 15 million dollars, near Pittsburg, Pa.

Page 98. *Recovering Tar and Ammonia in Carbonizing Coal, etc.*—Another patent of Brunck's is Ger. P. 289519.

Page 137. *Removing Tar and Ammonia from Gases.*—C. Otto & Co. (B. P. 12818, 1914) cool and wash the gases with cold water sprayed in the direction opposite to that in which the gases move. The cold water washes the tar out, and absorbs more and more ammonia on its way downwards, until it arrives at about the middle part of the washer. In the lower part of this, owing to the action of the hot gases, the volatile ammonia is expelled again from the water, so that this finally issues from the washer charged only with fixed ammonia compounds. In the middle part of the apparatus there is a zone where the washing-water has the highest contents of ammonia possible under the circumstances. If water is continuously withdrawn from this zone at such a rate that the quantity of ammonia removed in it per unit of time is substantially the same as is introduced during that time by the crude gases entering the washer, the process is made continuous. The water thus removed is separately removed from the tar and led directly to a still, to be worked up in known manner. The hot washing-water running away from the bottom of the washer contains, beside the tar, the fixed ammonia compounds. After the tar has been separated, this water is pumped to a cooling-tower, where such a quantity of it is evaporated as corresponds to the quantity of water precipitated in the process, so that there is no effluent beyond the water running away from the still. In order to avoid any loss of ammonia with the gases issuing at the top of the washer, these gases are passed through another washer fed with the same quantity of cold fresh water as is passed into the still. The water running over the cooling-tower becomes richer in fixed ammonia compounds, and is used over again, a portion of it being always conducted into the still with the water passing thereinto.

Page 138. *By-product Coke-ovens.*—According to *Chem. Trade J.*, 1915, p. 325, the La Belle Iron Works, Steubenville, Ohio, U.S.A., have started the erection of 94 Koppers by-product coke-ovens, with a daily capacity of about 1000 tons of blast-furnace coke. His German patents are Nos. 254014, 260317, 272601, 279550.

Recent patents for by-product coke-ovens:—

Bishop, U.S. P. 1166175.

Dr C. Otto & Co., Ger. P. 287234.

Page 157. *The recovery of benzene, toluene, etc., from coke-oven gas* by the use of light creosote oils is thoroughly discussed by an "expert" in *J. Gas Lighting*, cxxxi., pp. 502-503 (1915).

Heinrich Hirzel, G.m.b.H. (Ger. P. 290119), treats the hot coke-oven gases, before passing them into the benzol-washers, into special washers, provided with cooling-arrangements, in which benzol and naphthalene are washed out at the same time.

Page 167. *Recovery of By-products from Coke-ovens.*—At the British Association Meeting in 1915 the president (W. A. Bone) said that it was in the public interest, if Government fixed a time beyond which no coke-ovens were allowed to be worked without recovery of by-products, except by special permission of the Government, which should be accorded only in particular circumstances.

According to the U.S. Geol. Survey (quoted in *J. Soc. Chem. Ind.*, 1916, p. 299), the output of benzol and other light oils from by-product coke-ovens in the United States in 1915 amounted to 13,942,763 gall., together with 761,256 lb. of naphthalene. 6,620,093 gall. of oils were refined at the place of recovery, and yielded 4,833,939 gall. 100 per cent. benzol, 1,315,727 gall. toluol, and 470,425 gall. solvent-naphtha. This took place in thirty-one establishments with 4,933 by-product coke-ovens, in which between eight and nine million tons of coal were carbonized.

Retorts for the carbonization of coal are described in Duckham's B. P. 13935, 1914. They are made of steel or sheet-iron, considerably wider than deep, with vertical sides, and the top and bottom arched to the same curvature. They are arranged alternately with heating-flues in a vertical column, built of channel-iron bars which constitute the sides of the retorts and flues, and of arched plates held at the edges between the bars to constitute the tops and bottoms of the retorts and flues.

A description of *the modern carbonizing systems in America* is given in the *Trans. Intern. Gas Congress*, 1915 (quoted in *Abstr. Amer. Chem. Soc.*, 1916, p. 383).

Page 184. *Recovery of Toluene in the manufacture of Carburetted Water-gas.*—Sterne states in the *Journal of Industrial and Engineering Chemistry* (abstracted in the *Chem. Trade J.*, 1915, lvii., p. 410) that toluene may be recovered on a commercial scale in the manufacture of carburetted water-gas. In the service pipes of the gas-works at Kingston, Ontario, where carburetted water-gas is made with anthracite coal in the generator and Pennsylvania crude petroleum in the carburettor, during a very cold winter a pale amber liquid condensed, of sp. gr. 0·740, of which 95 per cent. distilled below 120°, and 99 per cent. below 130°. On careful fractionation this liquid yielded 75·88 per cent. paraffins, 1·62 per cent. olefins, and 22·5 per cent. aromatic compounds, consisting of about 12 per cent. benzene and 10 per cent. toluene. These might be separated, retaining the toluene and returning the benzene for illuminating and heating purposes.

Page 184. *Production of Benzene, Toluene, Xylenes, from Borneo Petroleum Oil.*—According to the *J. Gas Lighting* (quoted from *Chem. Trade J.*, 1916, p. 2), Borneo oil has been for a long time utilized in Germany for the production of benzene, toluene, xylenes, etc. One works at Rotterdam treats several tons per day of Borneo distillate containing from 15 to 20 per cent. of aromatic hydrocarbons, and representing about 1 per cent. of the crude oil. The aromatic hydrocarbons thus obtained are not pure; the toluene always contains some 30 or 40 per cent. of paraffin hydrocarbons.

Page 194. *Benzol and Toluol from Petroleum by the Rittman Process.*—According to *Chem. Trade J.*, 1915, lvii., p. 503, the U.S. Department of the Interior has cancelled a contract with the Ætna Explosives Company of New York, whereby that company agreed to expend a sum of not less than £40,000 on the development of the Rittman process, since such encouraging results had been obtained with that process that the company felt justified to erect plant for it on a commercially operative basis.

Rittman himself (*J. Ind. Eng. Chem.*, 1915, pp. 1014 *et seq.*) reports on the utilization of aromatic hydrocarbons derived from "cracking" petroleum. He concludes from his experiments that these hydrocarbons may be utilized for the preparation of nitro-products without being brought to a high degree of purity. The foreign substances not easily removable are paraffins, and these are not affected by reagents of sufficient vigour to transform the aromatics quantitatively into mono-nitro products. These compounds may be separated in a high degree of purity by a simple process of distillation. The mononitrotoluene prepared by the method indicated may be readily converted into trinitrotoluene, which, when washed with hot water, satisfies the ordinary commercial specification of a melting-point of 75°.

A paper on this subject, by Rittman and Egloff, is found in *Met. and Chem. Eng.*, 1916, xiv., p. 15 (abstr. in *J. Soc. Chem. Ind.*, 1916, p. 169); another paper, by Egloff and Twomey, in *J. Phys. Chem.* (abstr. in *J. Soc. Chem. Ind.*, 1916, p. 296).

Page 194. *Production of Motor-spirit, Benzol, and Toluol from Crude Petroleum or Petroleum By-product Oils.*—A process for producing motor-spirit by "cracking" heavy hydrocarbons is described in various patents of W. A. Hall (B. Ps. 24491, of 1913, 437 and 2948, of 1914; Fr. P. 467381). It consists in cracking the hydrocarbon oil at a temperature upward of 600°, separating from the product of the operation by fractional condensation the gases and the liquids volatile at about 200°, and condensing such vapour and gases together under pressure. According to the *Scientific American* of 1st May 1915, the oil is fed at a rate exceeding 70 gallons per hour through tubes of a total length of 300 feet, at a pressure of 50 to 75 lb. The speed of the vapours is over 5000 feet per minute. The oil is first vaporized in a coil, preheated in the flue by the waste heat of the products of combustion from the furnace. The temperature in the centre of the tubular coil is about 550°. The vapours then pass to a vertical pipe about 12 in. wide and 12 ft. high, entering through a confined throttle and impinging upon a baffle, whereby the speed of the vapour flow is reduced to a nominal rate. The temperature rises in that tube notwithstanding the reduction of pressure to atmospheric pressure, and a large amount of cracking takes place. The vapours pass through dephlegmators, and the uncondensed part then passes to a mechanical compressor, working at 70 to 100 lb. per square inch, and then under the same pressure through a cooler, where they are condensed to motor-spirit, the uncondensable gas passing on to a holder. A plant has been erected in England, with a capacity of 6000 gall. of motor-spirit per day; it has been taken over by the British Government, and is in full operation. Chandler (*J. Soc. Chem. Ind.*, 1915, p. 1182) describes some experiments he had made on Hall's process. The raw material was the "gas-oil" or "petrolite" of the Standard Oil Company, of sp. gr. 0·81 at 11° C., boiling-point 130°. From 18·97 litres of this material he obtained on the first passage through the apparatus, 10·6 litres motor-spirit, sp. gr. 0·77 at 11°, initial b. pt. 26°; 6 litres light residuum, 0·65 litre heavy residuum, 46·5 cub. ft. fixed gas. The 6 litres light residuum was passed through the coil again, and yielded 2·7 litres motor-spirit; total, 13·3 litres, or 70·6 per cent. of the original oil. No experiments were made to ascertain the percentage of benzol and toluol contained in the products. The motor-spirit was tested on an automobile engine, and it was found that one gallon of it did the work of 1·18 gall of gasoline at 1600 revolutions per minute; of 1·34 gall. at 1400 revolutions, and of 1·31 gall. at 1200 revolutions per minute. There was no noticeable difference in the behaviour of the liquids either in ease of starting, or absence of black smoke, or soot deposit in the cylinders.

Page 228. *The properties of benzol from coke-oven gas* have been investigated by G. Taylor (*J. Gas Lighting*, 1915, cxxxii., p. 639; *J. Soc. Chem. Ind.*, 1916, p. 166).

Page 231. *Differentiation of Coal-tar Benzene (Benzol) from petroleum Benzine.*—According to Mix (*Kolloid-Zeitsch.*, 1915, p. 7), a deep-red resin extracted from Sumatra dragon's blood, called "dracorubin," may be used in the form of coloured test papers, for distinguishing benzol from benzine. It is inactive in the cold towards benzine, but gives a deep coloration with benzol. (This paper is abstracted in *Z. angew. Chem.*, 1915, ii., p. 592; and *J. Soc. Chem. Ind.*, 1916, p. 167.)

Page 243. *The vapour-pressures of naphthalene* in air and coal-gas have been determined by J. S. G. Thomas (*J. Gas Lighting*, cxxxii., p. 701; *J. Soc. Chem. Ind.*, 1916, p. 166).

Page 255. *Solubility of Naphthalene in Ammonia.*—According to Hilpert (*Z. angew Chem.*, 1916, i, p. 57) naphthalene has the following solubilities in pure water, and in such containing ammonia, up to anhydrous NH_3:—

Percentage of NH_3	0	5	10	25	100
At 0° . .	0·019	0·030	0·042	0·064	33 per cent.
„ 25° . .	0·030	0·044	0·074	0·162	120 „

The pressure of pyridine increases the solubility of naphthalene; that of phenol has no effect. The organic impurities present in ordinary ammonia do not seem to alter the solubility of naphthalene, that of CO_2 and H_2S decreases it. On distilling ammonia containing naphthalene, the escaping vapours contain all the more naphthalene the higher the temperature, which influences its separation in the conduits. Anyhow, it is advisable not to allow the temperature of the pipe-conduits to fall below 30°, or else to interpose a cooled space for the separation of the naphthalene.

Page 275. *Acidic Properties of Alkyl-substituted Phenols.*—According to the investigations of Boyd and Marle (*J. Chem. Soc.*, vol. 105, p. 2117; vol. 107, p. 1538) the alkyl-substituted phenols (cresols, xylenols, etc.) are less acidic than phenol itself. The alkyl group is most effective when in the ortho-position with respect to the hydroxyl group, slightly less effective in the para-position, and much less effective in the meta-position.

Page 344. *The fuel efficiency of tar* is discussed by Moore in *Chem. Trade J.*, 1916, p. 235.

Page 360. *Coal-tar is employed for impregnating paper*, in order to make it watertight and to increase its strength and pliability. A prescription for this purpose is:—Mix 100 parts gas-tar, in the heated state, with 10 parts of mineral oil, add 10 parts sodium carbonate, pass the unsized paper through the hot bath, remove the excess of the liquid by pressing, and dry the product by hanging it up or by passing it over hot rollers.

Page 360. *Production of a Binding-Material for Coatings, etc., from Coal-tar.*—The Soc. anon. des Combustibles Industriels (Fr. P. 476362) heats the tar to remove ammoniacal liquor and light oils, and then to 120° to 250° in a rapid current of an inert gas. The distillate is freed from naphthalene by decantation, and incorporated with the undistilled residue. The heavy oil thus obtained is thickened by polymerization by means of a current of oxidizing gas, at a temperature below 250°. The product constitutes an excellent binding-material for coatings used in the metallurgical industry.

Page 368. *Tarring Macadam Pavement.*—Hobbs (B. Ps. 18354 and 18355, 1914) describes drying, mixing, and agitating machines for tarred macadam.

Page 371. *Treatment of Coal-tar.*—Davies[1] and Windsor-Richards have obtained for their process, mentioned in the text, the Ger. Ps. 274639 and 277602.

Page. 385. *Removing Tar from Hot Distillation-Gases.*—A further patent of the Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft is Ger. P. 284971.

Page 392. *Dehydration of Tar.*—E. V. Chambers (*J. Gas Lighting*, 1915, cxxxii., p. 261) states that by means of a centrifugal machine it is possible to reduce the water-content of the tar to 1 per cent., and to reduce the free carbon; but neither the volatile low-boiling hydrocarbons (benzene and toluene) nor the tar acids are thereby removed. The distillation process is free from these objections. The intermittent distillation process has several disadvantages from which the continuous process is free. Three qualities of "prepared tar" are specified by the Road Board, and may be obtained by distilling the tar until the residue has the temperature specified, viz.: for road spraying, 230°; for tar macadam, 260°; for pitch grouting, 288°. He gives a diagram of the Hird, Chambers & Hammond continuous dehydration plant, and quotes the results obtained therewith.

Wardell (*J. Gas Lighting*, 1915, p. 375; abstr. *J. Soc. Chem. Ind.*, 1915, p. 1238) describes the "Hird" continuous plant to deal with 20 tons tar per day, consisting of a rectangular steel still, fitted with longitudinal steel tubes and baffle-plates. The dehydration is complete when working at 260°.

Ammann (Fr. P. 475665) removes the ammoniacal liquor from coal-tar by spraying it into the upper part of a tall cylinder, wherein it meets an ascending current of hot air.

Page 393. *Purification of Coal-tar by treating it with Atmospheric Oxygen at a temperature of* 120°.—The Bayerische Hartstein-Industrie Aktien-Gesellschaft at Würzburg (Ger. P. 287236) divide the tar into thin jets and pass these through a space in which hot air ascends. The division of the tar may be effected by two or more concentrically arranged drums, which are perforated by many fine holes and revolve very quickly. By this process the ammoniacal liquor is completely evaporated and any oils contained in the tar are intimately mixed with the pitch.

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[1] This name is in the text wrongly spelt "Davis."

Page 396. *Preliminary Treatment of Raw Tar previous to its Distillation.*—The Rütgerswerke Aktien-Gesellschaft (Ger. P. 287962) remove the ammonium salts from coal-tar by heating it with aqueous liquids before the distillation. As such liquids they employ solutions of alkalis, alkaline earths or bicarbonates, with which the tar is thoroughly mixed and heated up to 90° to 100°, whereby the ammonium salts are decomposed; the solution formed is separated from the tar before its distillation. The vapours of ammonia and light oils formed during the heating are condensed in the usual way.

Page 408. *Tar-stills.*—Crossley and Brighten (B. P. 19392, of 1914) employ a still with its neck lagged with asbestos, and with a constricted opening controlled by a valve whose position can be adjusted and indicated. A low-pressure safety-valve is also provided.

Page 409. In order to avoid the trouble caused in the distillation of tar containing water by frothing over, Hoddick and Röthe (Ger. P. 287961) employ a specially shaped still.

Page 409. *Special descriptions of Tar-stills.*—Krickhuhn (Ger. P. 288702) combines two stills in such a way that the second still is placed beside the first, and is heated by the waste fire-gases of the latter; through the lower part passes a pipe through which flows the distillation residue (pitch) of the first still.

Page 458. Kubierschky's washing and distilling columns, described in the text, are described in detail, and very favourably reported upon by Borrmann in *Z. angew. Chem.*, 1915, xxviii., pp. 377-388 (abstr. in *J. Soc. Chem. Ind.*, 1915, xxxiv., p. 1232).

Page 468. *Distillation of Tar under Vacuum.*—Neumann (B. P. 20353, 1914) describes a receiver for use in vacuum distillation, by means of which portions of the distillate can be discharged at short intervals.

Page 494. *Wilton's Continuous Still.*—Livesey (*J. Gas Lighting*, 1915, pp. 373 *et seq.*; abstr. *J. Soc. Chem. Ind.*, 1915, p. 1238) describes the working of this still, especially the treatment of tar for toluol extraction.

Page 535. *Machinery for grinding and loading hard pitch* is described by Hill in Ger. P. 286243, B. P. 13546, 1915; for the production of hard pitch grains, by the Barrett Manufacturing Co. in Ger. P. 286549.

Page 539. Robert and Irinyi (Ger. P. 290798) employ pitch-dust for firing purposes.

Page 547. *Manufacture of Briquettes by means of Coal-tar Pitch converted into Dust.*—Fohr and Kleinschmidt (Ger. Ps. 263158, 284783, 289069) describe an apparatus and process for the preparation of patent fuel by means of coal-tar pitch or asphalt. Their process is described in detail by Dach in *Glückauf*, 1915, No. 12. The pitch, without being previously broken up, is heated first by a steam-coil to 100°, and then by direct fire to 160° to 170°, so as to be in a perfectly liquid state. In this state it is run into a steam-heated dust-producer, where it is converted into dust by means of high-pressure air, heated by steam, and blown into a horizontal, slightly inclined, mixing-drum, in which it solidifies, while still suspended in the air, forming an extremely fine, soot-like dust. In that slowly revolving mixing-drum, which contains lifting plates, the coal-dust and the pitch-dust are intimately mixed; the mixture is thoroughly kneaded by well-known machinery whilst being treated by superheated steam, and at last gets at a temperature of 55° to 80° into the presses. This process, as shown by practical trials at the Engelsburg pit of the Bochumer Verein, has several advantages over the old process of manufacturing patent fuel. To begin with, it does away with the necessity of grinding the pitch, an operation leading to frequent repairs of the mills and to great molestation and injury to the health of the men. Secondly, it admits of the application of soft pitch, whilst the old process requires hard pitch; soft pitch is as a binding-agent superior to hard pitch. Where the latter cannot be avoided, on account of the awkward circumstances connected with the transportation of soft pitch, the hard pitch admits of adding some tar. Thirdly, and principally, the new process causes a thoroughly uniform and intimate mixture of the coal-dust with the pitch-dust. At Engelsburg, where for the old process 5·61 to 5·68 per cent. pitch are required, the new process can be carried out with

4·3 per cent. pitch. To deduct from this economy in the matter of pitch is the cost of the steam in the new process; but this is only a fraction of the saving in pitch, and the cost of labour is the same in both cases. Fohr and Kleinschmidt have obtained for this process further patents, viz., in Italy, No. 137514; France, 461281; Belgium, 259176; Portugal, 8900; Spain, 56143; U.S.A., 1123719; Sweden, 37463; Austria, 69238 and 70372; Hungary, 63816. In March 1916, applications for patents were pending in England, Russia, and Norway.

Page 547.—*The briquette and tar-distilling plant* at the Nürnberg gas-works is described by Terhaerst (*J. Gasbeleucht.*, lviii., 300; *Amer. Abstr.*, 1915, p. 2089).

Diamant-Brikettwerke, Berlin, Ger. Ps. 280554, 287372.

Page 549. *Refined tar* and its use for macadam roads are discussed by Sharples in *Met. Chem. Eng.*, xiii., p. 918 (1915).

Page 555. *Distinguishing Natural and Artificial Asphalts.*—Marcusson (*Mitt. k. Materialprüf*, 1914, xxxii., p. 419-432; *J. Soc. Chem. Ind.*, 1914, p. 739; 1915, p. 1235) describes the determination of natural asphalt in admixture with coal-tar asphalt, by means of strong sulphuric acid, which converts the coal-tar asphalt into water-soluble sulphonic acids, and by other means.

Page 562. *Use of Asphalt for Coating Stones.*—Semmler (Ger. P. 289176) prevents the disintegration of slabs and stones, obtained by casting liquid scoria into moulds, by providing them with a coating of asphalt or tar before cooling. The impregnation may be made in a vacuum or under pressure. The impregnated smooth stones may be rendered rough by sprinkling them with sand. The coating may be produced either by dipping the stones into the impregnating mass, or by squirting or painting.

Page 563. *Utilization of Pitch.*—T. Glover (*J. Gas Light.*, 1916, p. 249; *J. Soc. Chem. Ind.*, 1916, p. 299) has found that the carbonization of coal with addition of 5 per cent. of disintegrated pitch gives good results both in gas-retorts and coke-ovens. Every ton of pitch yields 10,666 cub. ft. of gas and 12·14 cwt. coke. Some trouble was experienced when working with 10 per cent. of pitch, and with 15 per cent. of pitch the pipes were blocked.

Page 572. *Carbon powder is obtained from pitch* by Evans and Mitchell (B. Ps. 24313, of 1914, and 8901, of 1915) by shaking the pitch with a weak solution of caustic alkali in a closed vessel at about 100°, and then with naphtha at about 100°.

Page 660. *Lysol.*—According to *Chem. Ind.*, 1916, p. 61, William Pearson, the manufacturer of "Creoline" (p. 658) has made use of the state of war for having the patent and trade mark for lysol transferred to himself.

Page 688. *Pickling Timber.*—Loud (U.S. P. 1151204) describes the impregnation of wood, treating it first in a vacuum, then covering with a thin layer of the impregnating liquid, forcing this into the wood by increasing the air-pressure, and removing the excess of liquid by suction.

Page 725. *Manufacture of Carbolic Oil.*—Raschig (*Z. angew. Chem.*, 1915, i., pp. 409 *et seq.*) makes a very important communication on this subject, founded on his own practical experience. He states that before the war most of the carbolic acid required for German consumption was manufactured by working up crude carbolic acid, imported from Great Britain. This came about by the fact that the British coal-tars are very rich in carbolic acid, and that they were produced in much larger quantities than in Germany, owing to the much greater extension of the coal-gas industry. About the end of the last century Germany produced hardly one-third of the coal-tar produced in Great Britain, and, moreover, containing much less carbolic acid.

This state of matters has been changed by the extension of the by-product coke-ovens. Owing to this, Germany nowadays produces at least as much coal-tar as Great Britain. The coke-oven tars certainly are rather poor in carbolic acid, but already before the breaking out of the war, about one-third of the German tars was worked for carbolic acid. Since the commencement of the war, the importation of British crude carbolic acid has ceased, whilst more carbolic acid (and cresols) have been required for disinfecting purposes and for the manufacture of explosives. The state of matters will be even worse after the conclusion of peace, for there is even a greater scarcity of phenols in the neutral countries, both Germany and England having forbidden the exportation of phenols. Thus, *e.g.*, the price of carbolic acid in the United States is twenty times higher now than just before the war.

It is, therefore, a duty of the German manufacturers to work at the complete extraction of the carbolic acid existing in the German tars. To begin with, the arrangements must be made for producing a tar-oil fraction rich in carbolic acid. Such a fraction is the so-called "carbolic oil," which distils between 170° and 200°, and contains from 25 to 35 per cent. substances soluble in alkali. A number of factories already extract the phenols by treating the oils with caustic soda, but this process is only profitable at larger works; for it involves recovering the caustic-soda solution by decomposing the sodium carbolate by carbon dioxide, and recausticizing the sodium carbonate by means of lime; and this pays only in a permanent style of working, such as is not feasible for a tar-works of medium size, say, those distilling less than 100,000 tons tar per annum. It will therefore be best to leave the recovery of the phenols to special factories which get from the tar-distillers the fraction of oils distilling at about 170° to 250°, of sp. gr. 1 to 1·02. These are allowed to cool down in large boxes, whereupon naphthalene, about 20 per cent. of the weight of the oil, crystallizes out, about the same quantity remaining dissolved in the liquid oil. This contains about 25 per cent. phenol and its homologues, but the latter are prevailing, and it is therefore necessary to distil it once more before the alkaline treatment. This distillation is best carried out by means of a fractionating-column, and at reduced pressure, using indirect steam of 6 to 8 atmospheres pressure. The distillates are collected either in receivers kept also under a vacuum, or, preferably, in open vessels placed about 40 ft. below the cooler, which permits of taking samples at any moment. The distilling-columns must have a considerable height, and be filled with dephlegmating-sieves or bells. Raschig uses columns 48 ft. high, filled with a special kind of sheet-iron rings, described in his German patent 286122, and sold by the name of "Raschig's rings." The columns must be well insulated against loss of heat, in order to prevent an undue condensation on the outside walls. Owing to the vacuum, the temperature of distillation is about 120°. At first an oil comes over, completely free from phenols, which after being purified by a little concentrated sulphuric acid is identical with Commercial Solvent Naphtha, No. II. (p. 920), and is sold as such. When the test of the distillate shows that caustic-soda liquor absorbs a few per cent. of it, the receiver is changed, and the oil is now collected as "carbolic oil," with 30 to 40 per cent. of phenols. When the percentage of these in the distillate has gone down to 20 to 25 per cent., the distillate separates naphthalene on cooling down to 15°; the distillation is now stopped and the still residue run into a cooler, where naphthalene crystallizes out, and the oil is worked up in the usual way.

Raschig indicates the following dimensions of the apparatus. A still containing 175 to 280 cub. ft. requires a column of 2 ft. inside diameter. The steam-heating apparatus within the still, for a steam-pressure of 6 to 8 atmospheres, should have a heating-surface of 85 to 108 superficial ft., or less with higher pressures. The cooling-worm should have a diameter of 4 ins. at the bottom, reduced to 2 ins. half-way up. If made of sheet-iron, it must possess a cooling-surface of 43 to 53 sq. ft.; if made of copper, half of this is sufficient. The amount of cooling-water for each operation is about 700 cub. ft. The cooling-surface of the dephleginator should be 43 superficial feet for columns of a height of 40 ft.; for columns of half the height, twice the dephlegmating surface must be allowed.

Attention must be paid to the perfect tightness of the running-off pipes; the slightest air-bubbles getting into these are magnified by the vacuum to such an extent that they interfere with the course of the work. Otherwise the distillation is carried on quite smoothly, at 80° to 100° below the work done at ordinary pressures, without the decompositions occurring already at 200°. Whoever has made himself familiar with working at a vacuum will never return to the old style.

This apparatus also affords an opportunity of working up the "light oil" passing over in the distillation of coal-tar between 70° and 160°. In the usual style of work this oil, which contains about 10 per cent. phenols, is treated with caustic-soda liquor, and the sodium carbolate is decomposed by sulphuric acid, or run away to waste. This is unnecessary if a vacuum-column is provided, in which the "light oil" is first distilled at the ordinary pressure up to the point where the benzol and toluol have passed over, and only later on with a vacuum; thus the phenols of the light oil, which up to the present are mostly lost, are also recovered, and in the same way they can be extracted from the crude benzol obtained from coke-works.

In the same *Zeitschrift f. ang. Chem.*, p. 468, the Deutsche Teerprodukten-Vereinigung states that Raschig's paper does not contain anything hitherto unknown to practicians in that domain; to this Raschig replies that the results quoted by him have been only recently obtained by the application of long fractionating-columns, filled with Raschig's patented rings (p. 1633).

Page 765. *Synthetical Production of Carbolic Acid.*—In *J. Ind. Eng. Chem.*, 1916, p. 172, it is stated that synthetic carbolic acid had been manufactured by the Semet-Solvay Company at Syracuse from benzol in 1900 and the following years, in quantities up to 2500 lbs. daily, for conversion into picric acid. *Ibid.*, 1915, p. 686, Ney discusses the synthesis of phenol.

Page 786. A Committee of the American Wood Preservers' Association has issued rules for the quality of creosote for impregnating wood pavement (quoted in *Z. angew. Chem.*, 1916, iii., p. 234).

Page 823. *Carbolic Acid Statistics.*—According to Stone (*Oil, Paint, and Drug Reporter*, lxxxviii., No. 16, 1915; *Chem. Ind.*, 1915, p. 336), from 8 to 10 million pounds carbolic acid are consumed in the United States per annum, mostly for the manufacture of picric acid as an explosive. Only the factory of Thomas A. Edison, which has a daily production of 12,000 lbs. carbolic acid, does not work for purposes of warfare.

Page 830. *Purification of Crude Naphthalene.*—The Gesellschaft für Teerverwertung, Duisburg (Ger. P. 289945), heat the pressed crude naphthalene to 200° in a wrought-iron retort, provided with an empty top-column, a cooler and a receiver. Into the heated mass air is pumped for ten hours; the 10 to 15 per cent. of the naphthalene carried away by the air are used up with the next operation. The portion remaining after the air treatment on distillation furnishes pure, white naphthalene.

Page 843. *Estimation of Naphthalene by Picric Acid.*—Eyndhoven (*J. Gasbeleucht.*, 1916, p. 107) recommends for the estimation of naphthalene by picric acid the method of Rutten (*ibid*, 1909, p. 694; cf. *supra*, p. 843), as modified by Bunte (*ibid.*, 1912, p. 1260), viz., absorption by a standard solution of picric acid, to which a solution of potassium iodide and iodate has been added, and titrating the liberated iodine by means of sodium thiosulphate and starch solution.

Hilpert (*Z. angew. Chem.*, 1916, i., p. 58) shows that an addition of ether in testing naphthalene by picric acid is advantageous. He proceeds as follows:—The crude naphthalene (up to 0·2 g.) is dissolved in 30 c.c. ether and added to 50 c.c. of a titrated, about $\frac{1}{20}$-normal picric-acid solution, in a 200 c.c. flask, closed by a cork, perforated by a glass tube with a curved capillary inside end. After shaking for two minutes, the ether is sucked off by a vacuum, until the liquid has cooled down; the liquid is warmed up to 30°, and again treated with a vacuum until the ether is quite evaporated. The liquid is allowed to stand for two hours at ordinary temperatures, or ten minutes in ice; the precipitated picrate is filtered off, washed with 5 c.c. ice-water, and titrated with decinormal caustic-soda solution, litmus serving as indicator. The author subjoins his observations on the behaviour of naphthalene picrate.

Page 852. *Applications of Naphthalene.*—Franz Fischer (*Ber.*, 1916, p. 252) studied the action of aluminium chloride on naphthalene. This action had been already studied by Friedel and Crafts in 1885 (*Comptes rend.*, C., p. 692), by Homer (*Soc.*, xci., p. 1103) and Scholl (*Ber.*, 1910, p. 2202), but they employed very large quantities of aluminium chloride (from 25 to 400 per cent. of the naphthalene); whilst Fischer shows that on heating under pressure in an autoclave to 280° to 330° already 4 per cent. aluminium chloride suffice for converting 40 per cent. of the naphthalene into a mixture of liquid hydrocarbons, part of it combining with hydrogen taken from another part of the naphthalene. The oils obtained could be burned, but required a stronger supply of air than Russian petroleum to prevent the formation of soot.

Page 852. *Statistics for Naphthalene.*—According to Stone (*loc. cit.*), before the great European War the yearly production of naphthalene in the United States has been about 2½ million pounds, but has now risen to 7 million pounds. The normal consumption of it is about 9 million pounds per annum.

Page 893. *Utilization of Acid-tar from the purification of Benzol.*—The "Phœnix", Aktien-Gesellschaft für Bergbau and Hüttenbetrieb at Gelsenkirchen (Ger. Ps. 289162 and 289524) mix the waste acid from the purification of benzol with tar-oils, washing oils, or coal-tar, add to this ammoniacal liquor in which part of the ammonia is combined with hydrogen chloride, and blow steam through this mixture, whereby benzol, its homologues, and hydrogen chloride are driven out and can be recovered, ammonia remaining behind as ammonium sulphate.

Page 942. *Synthetical Toluene.*—Sifton and Harding Bros. (B. Ps. 8886 and 9437, 1915) prepare toluene by the action of methylic chloride on benzene, in the presence of aluminium chloride and iron turnings as catalyzers, at a temperature of 50°.

Page 950. *The Analysis of Commercial Benzols* is made by Spielmann and Wheeler (*Chem. News*, cxiii., p. 131) by a simple distillation and determination of specific gravities.

Page 971. *Determination of toluene* by fractional distillation. This is discussed in detail by H. W. James, in *J. Soc. Chem. Ind.*, 1916, pp. 236 *et seq.*

Page 1027. *Use of Benzol in lieu of Gasoline for driving Motor-cars.*—According to Stone (*loc. cit.*), up to 1915, benzol had not been used in America for this purpose in the way it is largely done in Europe, but it would now pay to do so, since its efficiency for that purpose is 25 per cent. above that of gasoline, which up to now is exclusively used for that purpose in the United States.

Page 1030. *Statistics of Benzol.*—According to Stone (*loc. cit.*), the production of benzol in the United States before the war of 1914, etc., has been only 3 million gallons per annum, but has now increased to about 15 million gallons.

Page 1055. *Preparation of Nitrogen.*—The Farbwerke, vorm. Meister, Lucius, and Brüning at Höchst (Ger. P. 286751) burn a mixture of ammonia gas and air, containing from 10 to 14½ volume per cent. of NH_3, in the presence of appropriate contact substances, whereby, besides nitrogen oxides and water, free nitrogen is formed, which can be isolated by taking out the nitrogen oxides and water. Their Ger. P. 289562 provides for adding to the mixture of ammonia and air some nitrogen, which prevents an injurious rise of temperature. According to their Ger. P. 289563, part of the air is replaced by oxygen.

Page 1059. *Processes for the Isolation of Nitrogen from Atmospheric Air*:—

Barschall, Ger. P. 259877.
Industrie - Gesellschaft für Sauerstoff- und Stickstoff-Anlagen, Fr. P. 446569.
Morrison, Fr. P. 452824.
Zeiss, Ger. P. 239575.
Nitrogen Co., Ossining, U.S. P. 999003; Ger. Ps. 258295 and 260804.
Blagborn, U.S. P. 1036788.
Kassner, *Chem. Zeit.*, 1912, p. 1187; 1913, pp. 1101, 1210.
Doherty, U.S. P. 1049812.
Aumont and Ville d'Arvay, Fr. P. 451307.
Acker, U.S. P. 1050902.
Simon, Fr. P. 466685.
Mewes, Fr. P. 456027.
Mettler, *Chem. Zeit. Rep.*, 1913, p. 476; 1914, p. 287.
Kausch, *ibid.*, 1914, p. 494
Brunt, *J. Amer. Chem. Soc.*, 1915, p. 1448.
Wallace and Wassmer, U.S. P. 1154145.
Hausmann, Fr. P. 474379.
Farbwerke Höchst, B.Ps. 3362, 1913; 9974, 1914; Ger. P. 286751; Fr. P. 453485.
Runge, B. Ps. 3420, 1914; Fr. P. 469793.
Bender, Ger. P. 280966.
Siemens and Halske, Aktien-Gesellschaft, Ger. P. 286514.
Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft, B. P. 28390, 1913.
Place, U.S. Ps. 1152044, 1152119, 1152120.
Winand, U.S. P. 1059584.
Wiley, U.S. P. 1056244.
Knowles Oxygen Co., *Chem. Zeit.*, 1913, p. 703.
Strutt, *Proc. Roy. Soc.*, Ser. A., 1915, p. 303.
Nitrogen-Gesellschaft, Fr. P. 468349.

Page 1060. *Preparation of Hydrogen.*—Further patents of the Badische Anilin- und Sodafabrik:—

B. Ps. 26700, 1912; 16494, 1914.
Fr. Ps. 439262, 453077, 463114.
Ger. Ps. 268929, 284176, 285703.
U.S. Ps. 1133087 and 1157669 (Bosch and Mittasch).

Page 1061. *Production of Ammonia from the Elements by means of Catalyzers.*—The Centralstelle für wissenschaftlich-technische Untersuchungen (Ger. P. 288496) employs as substratum for the catalyzers ten to twenty times their quantity of magnesia, magnesium oxide, or chromic oxide.

Page 1061. *Preparation of Hydrogen.*—Further patents of Messerschmidt:—

Ger. Ps. 258053, 263390, 263391, 267594, 266863, 268062, 268339.

Page 1064. *Preparation of Hydrogen.*—Further patents:—

Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft, B. P. 28390, 1913; with Dieffenbach and Moldenhauer, Fr. P. 414044; Ger. Ps. 267944, 270704, appl. B. 69856.
Dicke, Ger. P. 280964.
Ellis, U.S. P. 1092903, 1087937.
Lilienfeld, Ger. P. 276657.
Knowles, Swiss P. 67250.
Maschinenfabrik Fürth, Fr. P. 462394.
Benker, Fr. P. 461981.
Burdett, U.S. P. 1086804.
Levin, U.S. P. 1094728.
Mittasch and Schneider, U.S. P. 1128804.
Bergius and Aktien-Gesellschaft vorm. Moritz, Milch & Co., Ger. P. 259030.
Frank, Caro and Linde, Ger. P. 261735; Fr. P. 453187; Swiss P. 56594.
Le Morvan, Fr. P. 466309.
General Reduction and By-Products Co., Ger. P. 263025.
Schaefer, Ger. P. 289208, 290529; B. P. 16140, 1914; U.S. Ps. 1152196, 1152197; Fr. P. 461480.
Hlawaty, Ger. Ps. 275343, 275663, 277504; Fr. P. 453207.
Ephraim, Ger. P. 276718.
Pier, U.S. P. 1090874.
Farbenfabriken vorm. Bayer, Fr. P. 460859.
Dingler's Maschinenfabrik, Ger. P. 276953.
Rothe, U.S. P. 1083703.
Jul. Pintsch, Aktien-Gesellschaft, B. P. 28904, 1913.
Dempster, B. P. 16893, 1914.
Kewener, Ger. P. 290126.
Naher and Nöding, Ger. P. 290657.

Page 1064. *Carriage of Liquefied Hydrogen.*—According to *Chem. Zeit.*, 1913, pp. 647 and 757, liquid hydrogen is transported on railway trucks in steel cylinders 0·436 metre diameter and 3·55 metres long, tested for a pressure of 225 atmospheres, and practically exposed to a pressure of 150 atmospheres; they hold the equivalent of 2000 cub. metres of gaseous hydrogen.

Page 1087. *Synthesis of Ammonia by Nitrides.*—Further patents of the Centralstelle für Wissenschaftlich-technische Untersuchungen are:—

For the application of ruthenium: Swiss P. 62345. Their Italian P. 140597 describes special vessels for this purpose.

Their Ger. P. 288496 describes chromic oxide as a contact-carrier; Ger. P. 289105 magnesium oxide or carbonate for the same purpose. Their Ger. Ps. 287958 and 288666 prescribe carrying out the process in vessels made of or coated with silver; Ger. P. 286853 a specially constructed vessel.

Page 1088. *Synthesis of Ammonia.*—Hlawaty has made for his process, mentioned in the text, the Austrian patent application A4020—11.

Page 1094. *Synthesis of Ammonia.*—Classen's German patent for the process mentioned in the text is No. 289795.

Page 1096. *Preparation of Boron Nitride.*—

Weintraub (B. P. 12377, 1913; U.S. Ps. 1135232, 1157271).

Thomson-Houston Company (B. P. 14468, 1913).

Jevons (*Roy. Soc. Proc.*, 1914, xci*a.*, p. 120).

Page 1109. *Synthesis of Ammonia by means of Aluminium Nitride.*—Further patents of Serpek and of the Société Générale des Nitrures are:—

B. Ps. 1127, of 1914; 11271, 1915.

U.S. P. 1060640.

Ger. Ps. 239909, 246419, 266862.

Fr. Ps. 448924, 462464, 463390, 475908, 476121, 474820.

According to Wäser (*Chem. Zeit.*, 1915, p. 915) that Société already in 1912 possessed 283 patents, and further 87 had been applied for; but the economical results had not yet been entirely satisfactory at the close of the year 1915.

In *Proc. Amer. Inst. Elect. Eng.*, xxxiv., p. 2656 (1915), there is the report of a discussion on the Serpek process, in which it is stated that of the 250,000 h.p. available at Rjukanfos (Norway), only 3500 h.p. = 1·4 per cent. is actually utilized.

Page 1112. The preparation of *beryllium nitride* is described by Fichter and Brunner in *Z. anorg. Chem.*, xciii., p. 84 (*Chem. Zentr.*, 1915, ii., 1281).

Page 1125. *Investigations on the behaviour of Calcium Cyanamide* have been made by Morrell and Burgen (*J. Chem. Soc.*, 1914, p. 576), and Werner (*ibid.*, 1915, p. 715).

Page 1136. *Ammonia from Cyanamide.*—An extensive paper by Landis (*J. Ind. Eng. Chem.*, 1916, pp. 156 *et seq.*) describes in detail that process in general, and the contributions to it by himself in particular. (On p. 1138 his American patent 1149633 is erroneously mentioned as No. 1149653.)

Gui (U.S. P. 1164087) allows nitrogen to act on calcium carbide while mixed with a much larger amount of red-hot calcium cyanamide, which prevents formation of a compact mass during the reaction.

Page 1137. *The injurious effects of the manufacture of lime-nitrogen on health* are treated by Koelsch (*Vierteljsch f. off. Ges. Pfl.*, xlvii., pp. 326-350; *Chem. Zentr.*, 1916, p. 517).

Page 1137. *Preparation of Calcium Cyanamide* (*Lime-nitrogen*).—Patents have been further taken out for this by:—

Stickstoffwerke, Berlin, Ger. P. 258342.
Krauss, Kappen and Aktien-Gesellschaft für Stickstoff-dünger, Ger. Ps. 260469, 267514; Fr. P. 450435.
Greenstreet, U.S. P. 1052815.
M. Müller, Ger. P. 262473.
Zamore and Carlson, Norw. Ps. 23063 and 23064.
Stockholm's Superphosphate Fabrik, A. B. (*Chem. Zeit.*, 1912, p. 1297).
Zelasko, Ger. P. 273111.
Grube and Krüger, Ger. P. 279133.
M'Court and Ellis, B. P. 25629, 1912.
Patrouilleau, Fr. P. 475195.
Tommasi and Usines Electriques de la Lonza, Fr. P. 476294.
Ashcroft, U.S. P. 1163498.
Lidholm and The Dettifoss Powder Co., Ger. P. 274472.
Carlson, Norw. Ps. 23063 and 23064.
Kirchhoff, *Chem. Zeit.*, 191, p. 1058.
Pranke, *Chem. Zeit. Rep.*, 1913, pp. 333, 503.
Briner, *ibid.*, 1913, p. 665.
Kühne and Bredig, *ibid.*, 1913, p. 831.
Alby, *ibid.*, 1913, p. 143.
Brackett, *ibid.*, 1914, p. 430.
Hönigschmidt, *ibid*, 1914, p. 531.
Various, *Chem. Zeit.*, 1912—p. 1176; 1913—pp. 370, 515, 617, 787, 819, 924, 999, 1010, 1081, 1111, 1187, 1444, 1563; 1914—pp. 201, 408, 519, 520, 621, 641, 778, 1071, 1110, 1260.

Page 1145. *Synthetical production of Ammonia.*—In *Chem. Zeit.*, 1915, p. 915, Wäser reports on the economical success of the recently worked-out methods for the synthesis of ammonia. In January 1914, a selling union was made between the Badische Anilin- und Sodafabrik, the Deutsche Ammoniak-Verkaufsvereinigung, and the Oberschlesische Kokswerke und Chem-Fabriken Aktien-Gesellschaft. The first-named firm at the end of 1915 will produce about 150,000 tons ammonium sulphate per annum at their factory at Oppau, in Silesia, by the Haber-Rossignol process (p. 1070).

Page 1153. *Ammonia as a By-product in the manufacture of Beetroot Sugar.*—To the paper of Donath, abstracted in the text, remarks have been made in the *Deutsche Zucker-Ind.*, xl., 503, *Z. angew. Chem.*, 1915, ii., 563, to which Donath makes a reply in *Deutsche Zucker-Ind.*, xl., p. 845.

Viganó and Soldi's Ital. P. 135224 treats the recovery of ammonia from molasses-slops.

Page 1153. *Ammonia from Distillers' Washes.*—Kochendoerfer (U.S. P. 1165358) passes the nitrogenous gases produced by carbonizing distillers' wash through hot tubes lined with quartz or zirconium oxide, to produce cyanogen compounds and ammonia.

Page 1182. *Ammonia from Peat.*—Halvorsen (B. P. 17882, 1914) adds to peat acids or salts before heating under pressure to 160° to 300°, whereby a large proportion of the nitrogen present is converted into ammonia, and is recovered from the liquid. Suitable chemicals are hydrochloric, sulphuric, and sulphurous acid; ferric chloride and sulphate; chlorides of Ca, Mg, or Na; kainite and bisulphites; but not nitric acid or nitrates.

Further patents:

Testrup, Adam, Rigby, and Andrew, U.S. P. 1145095.
Nodon, Ger. P. 274346.
Rigby and Wet Carbonizing, Ltd., B. P. 18558, 1914.
Torfentgasungsgesellschaft Stauber, Ger. P. 290577.

Page 1204. *Recovery of Ammonia from Coal-gas Washing-water.*—Hilleke (U.S. P. 1163752) washes the gas with the water of condensation; the water is heated, and the gases passed through an acid bath, to form ammonium sulphate.

Page 1213. *Influence of Steam on the yield of Ammonia in gasifying Coal or Shale.*—Sachs (Ger. P. 274011); inaugural dissertation, Karlsruhe; *Chem. Zentr.*, 1915, ii., p. 1222) states that in the employment of little steam, 900°, in that of much steam, 800°, is the best temperature for gasifying the coal. The steam has a protecting influence against the decomposition of ammonia by heat. The gases are taken away from the interior of the coal, etc., by pipes, the temperature of which is kept low enough by cooling-devices to prevent any decomposition of the ammonia.

Page 1231. *Ammoniacal Liquor from Tar, by treating it with Hot Air.*—The Bayerische Hartstein-industrie Aktien-Gesellschaft, Würzburg (Ger. P. 287236) recovers the ammoniacal liquor present in the tar, the vapours being withdrawn by a fan.

Page 1234. *Statistics on the Recovery of Ammonia in Carbonizing Coal in Great Britain.*—According to Bone (*Chem. News*, 1915, cxii., p. 223), there was recovered in Great Britain:—

Year.	Tons of Ammonium Sulphate produced in	
	By-product Coke-ovens.	Gas-works.
1903 . . .	17,435	149,489
1908 . . .	64,227	165,218
1913 . . .	133,816	182,180

Page 1252. *Ammonia from Crude Heating and Lighting Gases.*—Dralle, *Z. angew. Chem.*, 1916, ii., 178.

Page 1264. *Composition of Gas-liquor from Vertical Retorts.*—Kropff (*J. Gasbeleucht.*, 1916, p. 158) analysed such liquor by Dyson's method (*supra*, p. 1277), and found in it:—

Total ammonia . . . . . . 16·39 grammes per litre.
Total sulphur . . . . . . 2·91 " "

	Grammes per litre.		
NH_4S .	3·84 =	1·28 NH_3 =	7·81 per cent. of the total NH_3.
$(NH_4)_2CO_3$.	36·48 =	12·92 " =	78·83 " "
NH_4Cl .	7·03 =	2·05 " =	12·51 " "
NH_4CNS .	0·53 =	0·12 " =	0·73 " "
$(NH_4)_2SO_4$.	0·28 =	0·04 " =	0·24 " "
$(NH_4)_2S_2O_3$.	0·19 =	0·11 " =	0·67 " "
$(NH_4)_2FeCN_6$	0·14 =	0·02 " =	0·12 " "

Page 1301. *Properties of Ammonia.*—Lewis and Adams (*J. Amer. Chem. Soc.*, 1915, xxxvii., p. 458) state the following amounts of calories as the free energy of the formation of NH_3 at 298°: for gaseous NH_3, −4740 cal.; for liquid NH_3, −3490 cal.; for NH_3 in aqueous solution, −7130 cal.; for NH_4OH in aqueous solution, −63,750 cal.; for NH_4, −19,895 cal.

Page 1329. *Storage of Ammoniacal Liquor.*—To prevent the loss of ammonia by the circulation of air above the surface of the liquor, Curphey (*J. Gas Lighting*, 1915, p. 424) covers it with a layer of paraffin oil, which also retards the formation of ammonium salts by oxidation.

Page 1358. *Manufacture of Liquor Ammoniæ.*—The paper of Hilgenstock is also found in *Amer. J. Gas Lighting*, 18th Oct. 1915, and *J. Gas Lighting*, 1915, cxxxii., p. 436.

Page 1467. *The use of nitre-cake in the manufacture of sulphate of ammonia*, in lieu of sulphuric acid, is advocated by the British Ministry of Munitions, by a circular issued in 1916 (*Chem. Trade Journ.*, 1916, p. 212; *cf.* Cooper, *ibid.*, p. 233).

Page 1484. *Ammonium Sulphate*, together with sulphur, is obtained by Bergfeld (Ger. P. 290509) from crude coal-gas by washing it, first with acid ammonium sulphite solution, and then with an alkaline sulphite solution.

Ammonium sulphate from coke-oven gases, according to Wiley (*J. Gas Lignting*, 1916, p. 257), is best obtained by the "semi-direct" process, described in *J. Soc. Chem. Ind.*, 1905, p. 839.

Page 1520. *Statistics on Sulphate of Ammonia.*—According to Bradbury and Hirsch, in 1915 the *United Kingdom* produced ammonia calculated as sulphate, from all sources (including that used in the manufacture of ammonia-soda, munitions, and for other chemical purposes): 423,000 tons; viz., gas-works, 173,000 tons; iron-works, 16,000 tons; shale-works, 58,000 tons; coke and carbonizing works and producer-gas, 176,000 tons. Of that quantity, England contributed 302,000 tons, Scotland 118,000 tons, and Ireland 3000 tons (*J. Soc. Chem. Ind.*, 1916, p. 114).

The exportation in 1913 was 328,238 tons; in 1914, 318,913 tons (*Chem. Ind.*, 1915, p. 547).

Page 1522. The *United States* produced in 1913, 195,000 tons, in 1914, 183,000 tons, of ammonium sulphate, of which 76 per cent. came from coke-works, and 24 per cent. from gas-works and other sources (*Chem. Ind.*, 1915, p. 550).

Page 1524. *Austria-Hungary* produced in 1912, 38,000 tons, in 1913, 45,000 tons of ammonium sulphate (*Chem. Ind.*, 1916, p. 53).

Page 1532. The Badische Anilin- und Sodafabrik (Ger. P. 290747) prepare ammonium chloride by the action of sulphuric acid and ammonia upon alkaline chlorides in presence of a limited quantity of water.

INDEX OF NAMES

AARLAND, 219
Aarts, 1231
Abderhalden, 370
Abegg and Riesenfeld, 1299
Abel, 701, 702, 703, 788
Abendroth, 1380, 1449
Accum, 19, 375
Acker, 1608
Addie, 171, 175, 1246, 1248, 1252, 1480, 1481
Adhikary, 1146
Adiassewich, 938
Adler, 1534, 1536, 1542
Adriaanse, 1380, 1448
Adrieenz, 227, 229, 269
Agricola, 1045
Ahrens, 213, 286, 290, 295, 296-97
Ahrens and Garbow, 295
Ahrens and Dennstedt, 293
Ahrens and Modzdenski, 215, 239
Aitken, 54, 91, 96
Aktien-Gesellschaft für Anilinfabrikation, 620, 1009
Aktien-Gesellschaft für Asphaltierung, 351, 555
Aktien-Gesellschaft für Kohlendestillation, 79, 98
Aktien-Gesellschaft für Kohlensäure-Industrie, 1406, 1407
Aktien-Gesellschaft für Stickstoffdünger, 1139
Aktien-Gesellschaft für Teer- und Erdöl-Industrie, 282, 285, 306, 467, 554, 617, 625, 626, 627, 663, 741, 856, 870
Aktien-Gesellschaft für Teerprodukte, 546
Albone and Boswell, 678
Albrecht and Müller, 844
Alby, 1611
Alder, 1023
Alex, 18, 20
Alexander, 283, 360
Alexander and M'Cosh, 171, 175, 1245
Alexeieff, 270
Al-Garitz, 1042
Alkali Inspectors, 1282, 1456, 1481, 1502, 1503, 1504, 1509, 1511, 1516, 1520, 1522
Allen, 269, 270, 636, 637, 695, 795, 797, 800, 808, 815, 817, 920, 953, 954, 960, 974, 1112
Allen and Angus, 178
Allner, 526
Altena, 688
Aluminium Industrie, Aktien-Gesellschaft, 1108, 1111
Alvisi, 1576
American Cyanamide Co., 1124, 1135, 1136, 1138, 1142
American Gas Engineers' Committee, 1026
American Railway and Maintenance of Way Association, 705
American Wood Preservers' Association, 1605
Ammann, 1598
Andernach, 360
Anderson, 19, 250, 251, 293, 294, 295, 296, 304, 1090
Anderson and Roberts, 1191, 1200
Andés, 361, 363
D'Andria, 1342
Andriesen and Scheidemantel, 1070
Andrlik, 1158
Angelucci, 1146, 1159
Angerstein, 633
Anschütz, 311
Anschütz and Eltzbacher, 251
Appolt, 88, 99
Arad-Csanad Railway Co., 690
Archbutt, 695
Archdale, 494
Archer, 328
Armengaud, 1114
Armstrong, 65, 66, 101, 146, 186, 187, 547
Armstrong and Miller, 66, 212, 215
Arndt, 1124
Arnold and Mentzel, 661
Arnold and Werner, 786
Arrol and Meikle, 1469
Artmann, 494, 663
Asboth, 293
Ashcroft, 1123, 1140, 1611
Atterberg, 188
Atwati, 166

Audouin, 137, 324, 455, 456, 460
Audouin and St. Claire Deville, 672
Auerbach, 253, 622
Aumont and Ville d'Avray, 1608
Aussig Chemical Works, 1147
Autenrieth and Beuttel, 801
Autogen and Werke, 1021, 1029
Avenarius, 605, 606
Avery, 327
Aydon and Shpakovsky, 323

BACH, 271, 788
Bachmann and Sulzer, 1380
Bäcker, 316, 323
Bader, 802
Badin, 1111
Badische Anilin- und Sodafabrik, 511, 822, 852, 882, 939, 1059, 1060, 1070, 1072, 1074, 1076, 1077, 1078, 1079, 1080, 1081, 1082, 1083, 1084, 1085, 1097, 1098, 1110, 1122, 1131, 1138, 1143, 1144, 1207, 1238, 1341, 1460, 1482, 1484, 1559, 1560, 1608, 1612, 1615
Badische Gesellschaft für Zuckerfabrikation, 1150
Baekeland, 814
Baeyer, 216, 221, 222, 286, 299, 300, 304, 813
Bailey, 1516
Bakelite-Gesellschaft, 814, 823
Baker, 1068
Bakerfield, 156
Balfour and Lane, 573
Ballantyne, 1449, 1473
Ballard, 462, 464, 477, 557, 758, 1336, 1489, 1491, 1496, 1512
Ballow, 244
Baltzer, 4, 6, 308
"Bamag." *See* Berlin-Anhaltische Maschinenbau Aktien-Gesellschaft.
Bambach, 1086, 1239, 1481
Bamberger, 1389
Bamberger and Bordt, 246
Bamberger and Chattaway, 261, 263
Bamberger and Hooker, 262
Bamberger and Kranzfeld, 260
Bamberger and Lodter, 246, 249, 258
Bamberger and Philip, 261
Bamberger and Strasser, 7
Bannow, 964
Barbet, 495, 729
Barbier, 249
Barboni, 1010
Barlen, 136, 410
Barnick, 80, 1450, 1478, 1530
Baroni, 659
Barrett Manufacturing Co., 1600
Barrow, 68, 455
Barrik, 1544
Barschall, 1608
Barth, 285, 1480
Barthe, 901
Basilius Valentinus, 1043, 1044, 1045
Basset, 636, 1095
Baswitz, 1013
Baudet, 821
Bauer, 56, 96, 98, 105, 117, 118, 581, 984
Baumann, 267
Baumé, 1043, 1527
Baur, 1112
Bay, 981, 983
Bayenthal, 180
Bayer, 608, 646, 1107, 1108, 1287, 1288, 1289
Bayer & Co., 1131
Bayerische Hartstein-Industrie, Aktien-Gesellschaft, 1598, 1613
Bayrische Stickstoffwerke, 1140, 1141
Bazzano e Zanardo, 1133
Beaulieu-Marconnay, 1519
Becher, 16, 17
Becher and Serle, 14
Bechi, 244, 254, 257, 259, 632
Beck, 495, 519
Becker, 519, 520, 522, 1505, 1506
Becket, 1135
Beckurts, 787, 798, 800
Beckurts & Otto, 817
Beda, 821
Bedson, 8, 294
Beguin, 1045
Behr, 547
Behr and van Dorp, 226, 251, 284
Behrens, 40, 89, 146, 228, 535, 561, 562, 566, 571, 573, 644, 685, 707, 733, 770
Beilby, 29, 30, 1183, 1208, 1305
Beilstein, 210, 236
Beilstein and Geuther, 1305
Beilstein and Kurbatow, 189, 214, 215, 216
Beimann, 1530
Bell, 97, 101, 304, 1182, 1290, 1516, 1555
Bendel, 1557
Bender, 1085, 1560, 1608
Bengough, 890
Benker, 1564, 1609
Benoist and Camolly, 718
Benson and Crites, 1385
Benut and Renant, 91
Berend, 300
Berger, 586
Bergfeld, 1056, 1614
Bergius, 1587
Bergius and Chemische Fabrik Aktien-Gesellschaft, Moritz, Milch & Co., 1069, 1609
Bergman, 1045
Bergmann, 546
Bergwerksgesellschaft Trier, 1237, 1358

Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft ("Bamag"), 60, 319, 385, 650, 684, 1024, 1237, 1336, 1339, 1351, 1353, 1357, 1358, 1373, 1374, 1382, 1391, 1450, 1475, 1476, 1478, 1530, 1538, 1587, 1598, 1608
Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft, Dieffenbach and Moldenhauer, 1609
Berliner Holzkomptoir, 657, 663, 903
Bernard, 316, 1274
Bernbeck, 1387
Bernhard, 361
Berninghaus, 459
Bernthsen, 301, 304, 1077, 1078
Bernthsen and Bender, 300, 301
Bernus, 542, 543
Berson, 1378
Bertelsmann, 39, 113, 1192, 1258, 1312, 1391, 1396
Berthelot, 64, 67, 213, 226, 229, 230, 233, 238, 239, 245, 246, 248, 251, 253, 263, 268, 309, 310, 313, 1029, 1574
Berthelot and André, 1271, 1316
Berthollet, 1045, 1303
Berzelius, 232, 1304
Besemfelder, 1152, 1253
Beslier, 1029
Bethell, 20, 376, 679, 680, 681
Beyling, 1019
Beyrom and Christopher, 95
Bial, 813
Bickerdike, 750
Bidet, 767, 937
Bidle, Shaw & Linton, 673
Bidley, 328
Biedermann and Jacobson, 289
Biehringer, 936, 982
Bielefeldt, 851, 1441
Bierotte, 811
Biet, 1044
Biétrix, 545
Bifalini and Vitali, 1576
Bilfinger, 712
Biltz and Marcus, 1051
Binder, 582
Binks, 1114
Birkeland, 1054
Birkeland and Eyde, 1048, 1075, 1103, 1562
Biron, 228
Bischof, 9
Bishop, 1592
Bizzarri, 283
Blackmore, 1094
Blagborn, 1608
Blairs, 1119
Blass & Son, 370, 607
Bloxam, 1129
Blum, 1438
Blumer, 813
Blythe, 684
Board of Trade, 1406
Bock, 540
Bockelberg & Sachse, 494
Bodländer, 817
Bodwell, 328
Boecking & Co., 1242
Boeddeker, 341
Boedtker, 938
Boehme, 975
Boerhave, 1308
Boerner, 1205
Boes, 243, 246, 271, 283, 301, 626, 769
Böhm & Co., 426, 483
Böhmer, 1517
Böhringer, 765
Boissieu, 191
Bokorny, 271, 607, 661, 813
Boleg, 603, 662, 709
Bolley, 200, 389
Bolton, 16, 314
Bolton and Wanklyn, 1159, 1204, 1240
Bolton and Watts, 18
Bolz, 1192
Bonardi, 1167
Bone, 1226, 1590, 1593, 1613
Bone and Jordan, 308, 626
Bonelli, 1517
Bonneau, 1359
Bonneau and Hasenfratz, 1358, 1488
Borchers and Beck, 1101, 1123
Bormann, 410, 458, 1599
Bornemisza and Kopal, 546
Börner, 1161
Börnstein, 39, 46, 256, 264, 279, 1286
Börnstein and Kleemann, 944, 993
Borrmann, 935
Bosch, 1072, 1083, 1138, 1482
Bosch and Mittasch, 1074, 1079, 1081, 1084, 1110, 1131
Bosnische Elektrizitäts Aktien-Gesellschaft, 1134
Bossche, 1320
Bossé, 1380
Boston Petroleum Heating Co., 327
Boswell, 678
Bott, 277
Boucherie, 679
Boudoin and Escarpit, 1146
Boult, 1087
Boulton, 148, 182, 455, 464, 504, 558, 668, 679, 680, 681, 682, 683, 684, 690, 697, 698
Bourgeoin, 11[illegible]3
Bouriez, 546
Bowden & Dodd, 712
Bowditch, 845
Bowen, 1448
Bower, 1333, 1495, 1548
Bowing, 546
Boye, Gebrüder, 677

Boyde and Marle, 1597
Boyen, 263, 275, 314
Boyle, 1044, 1045
Brackett, 1611
Bradbury & Hirsch, 31, 1614
Bradford Corporation, 1494
Bradley and Jacobs, 195, 624
Braeutigam, 294, 901
Bramwell, 1114
Brand, 1546
Brandenburg, 1457
Brandt, 330, 333, 335
Brassert and Bacon, 1380
Brauer, 1333
Braun, 362
Bray, de, and Rosetti, 328
Bréant, 681
Bredig, 1125
Bredig and Fränkel, 1132
Breitenlohner, 707, 881
Breitkopf, 1015
Breniman, 1113, 1121
Breslauer, 885
Brieger, 267
Brin, 1119
Briner, 1611
Brinck and Hübner, 826
Briner and Mettler, 1093
Brison, 1380
British Cyanides Co., 1551
British Cyanides Co., and Chance, 1548
British Ministry of Munitions, 1614
British Sulphate of Ammonia Association, 1513, 1518
Brix, 362
Brochet, 213, 214, 221, 238
Broex, 200
Bronn, 1294, 1389
Brönner, 19, 376, 425, 718, 732, 746
Bronnert, 1100, 1103
Brookmann, 576
Brosche, 1150
Brotherton and Wyld, 1476
Brown, 443, 1512
Brown and Shadinger, 519
Bruch, 1160
Bruckmann, 341
Bruhn, 216, 849
Bruhns, 1273
Brullé and Leclerc, 1159
Brunck, 61, 70, 72, 80, 92, 93, 97, 98, 145, 156, 307, 1236, 1241, 1243, 1327, 1380, 1472, 1591.
Brunel and Woog, 1068
Brunet, 1188
Brunner, 1308
Brunt, 1608
Buchanan, 578, 585
Buchanan and Maxted, 1061
Bucher, 1089, 1101, 1113, 1122
Bueb, 28, 46, 479, 598, 607, 608, 645, 1021, 1082, 1206, 1258, 1312, 1547
Bueb and Deutsche Continental Gasgesellschaft, 1557
Buess, 676
Buff and Hofmann, 1301
Buffett, 328
Buhl and Keller, 1159
Bühler, 822, 893, 1562
Bull, 92
Bunet, 1111
Bunsen, 9, 64, 1057, 1291, 1292
Bunsen and Playfair, 170, 1113, 1248
Bunte, 34, 50, 51, 52, 64, 186, 312, 316, 321, 322, 1008, 1022, 1065, 1204, 1606
Bunte and Grahn, 1162, 1580
Bunte and Eitner, 1015, 1410, 1412
Burdett, 1609
Buresch, 679
Burg, 262
Burgemister, 56
Burgess, 328
Burgess and Edwards-Ker, 1140
Burghardt, 910, 1568
Burkheiser, 1122, 1199, 1200, 1238, 1321, 1480
Burnett, 680
Burns, 317
Burrell and Robertson, 87
Burschell, 362
Burstall, 47
Burstell, 1336
Burt, 681
Burt, Boulton, and Haywood, 465, 504, 688, 703, 874
Bury, 52, 94, 161
Buser, 814
Busey, 1388, 1389
Busley, 341
Buss and Fohr, 852
Busse, 811
Butler, 546
Butterfield and Watson, 1160
Butlerow, 209
Byrom, Wigan, and Bennett, 55

Cabot, 470
Cady, 1294
Cahours, 234
Callenberg, 851
Calvert, 243, 269, 275, 732, 760, 762, 812, 815, 844, 1089, 1542
Cambria Steel Co., 80
Campbell and Boyd, 1193
Campion and Tenison Woods, 1568
Carey, 1561
Carl, 847
Carlson, 1126, 1576, 1611
Carnelly, 223, 264, 532

Caro, 68, 1055, 1056, 1088, 1126, 1128, 1129, 1130, 1178, 1179, 1180, 1181, 1219, 1220, 1221, 1233, 1523, 1576
Caro, Clemm, and Engelhorn, 68
Caro and Frank, 1123
Caro and Scheele, 1580
Carpenter, 1258, 1281, 1359, 1515
Carpenter and Claus, 1502
Carpenter and Linder, 1285, 1311, 1334, 1335
Carr, 31[illegible], 1359, 1450
Carré, 802, 1389
Carter, 62
Carulla, 1473
Carvès, 71, 72, 91, 92, 94, 95, 119, 127, 146, 178
Casella, 961
Caspari, Nydegger, and Goldschmidt, 1567
Caspers, 615
Cassal, 1148
Cassel, 1094
Casselmann, 823
Casthelaz, 791
Castner, 1164, 1305
Catchpole, 602
Cava, Soc. an., 498
Caventou, 219
Cedercreutz, 1556
Cellarius and Lehmann, 1382
Centralstelle für Wissenschaftlich-technische Untersuchungen, 1061, 1608, 1610
Chaligny and Guyot-Sionnet, 688
Chambers, 1598
Chambers and Smith, 97
Chameroy, 562
Chance, 1500, 1564
Chandelon, 800
Chandler, 1596
Chantard and Kessler, 823
Chapin, 794
Chapman, 171, 1246
Charitschkoff, 232, 992
Charnute, 692
Charpy and Bonnerot, 1112
Chateau, 1498
Chatfield, 1342, 1479, 1556
Chaumont, 534
Chemical Engineering Co., 393, 1450
Chemische, Fabrik Aktien-Gesellschaft, Hamburg, 304, 615, 627, 809, 894, 898
Chemische Fabrik Dr K. Albert and Behrend, 814
Chemische Fabrik Bettenhausen, Marquart & Schulz, 1483
Chemische Fabrik Brugg, 1555, 1557
Chemische Fabrik Flörsheim, 369, 710
Chemische Fabrik Griesheim-Elektron, 1063
Chemische Fabrik Gross-Weisandt, 555
Chemische Fabrik von Heyden Aktien-Gesellschaft, 1122
Chemische Fabrik Knoll and Co., 372
Chemische Fabrik Ladenburg, 737
Chemische Fabrik Lindenhof, 393, 409, 480, 564, 576
Chemische Fabrik Moritz Milch and Bergius, 1063
Chemische Fabrik Pommerensdorf, 1538
Chemische Produktenfabrik Pommerensdorf and Steger, 1154, 1232, 1238, 1239, 1482
Chemische Fabrik Salzkotten, 417
Chemische Fabrik Schering, 1575, 1578
Chemische Industrie Aktien-Gesellschaft and Wolf, 1194
Chemische Werke Ichendorf, 765
Chenier and Lion, 848
Chevalet, 1380, 1458
Christian, 698
Christiani, 267, 691
Christie, 1192
Chiard, 1168
Chur, 1359, 1378, 1480
Church, 234, 441, 519, 521, 526, 552, 581 584, 705, 706, 762
Church and Owen, 291, 296
Church and Weiss, 794
Church and White, 649
Chevalet, 59
Ciamician and Weidel, 305
Clark, 692, 1248
Clarke, 1202
Clarke, Chapman & Co., 1231, 1476
Classen, 286, 1094, 1610
Claude, 1051
Claudon and Morrin, 996
Claus, 684, 1193, 1500, 1501, 1502
Clayton, 17
Clegg, 18
Clessler, 819
Clift, 746
Clonkey, 795
Cnobloch, 1020
Coates, 710
Cobb, 1194, 1483
Cochrane, 970
Coehn, 1309
Coehn and Prigert, 1304
Coffey, 1416, 1418, 1422, 1439
Cohen, 228, 233, 234, 983
Cohn, 632
Coke-Oven Constructing Co. and Brown, 97
Colladon, 58
Collett, 1239, 1480
Collett and Eckardt, 1102, 1138, 1195, 1239, 1480
Collett and Norsk Hydro-Elektrisk-Kvaelstofaktieselskab, 1572
Collier, 658
Collin, 97, 98, 138
Colman, 921, 971, 992

Colman and Smith, 843
Colson, 1471, 1570
Coltness Iron Co., 173, 1251
Committee on the Supply of High Explosives, 992
Compagnie française Thomson-Houston, 1096
Compagnie Internationale de l'Oxygène, 1058
Compagnie Parisienne des Couleurs d'Aniline, 905
Conring, 547
Constam and Rougeot, 532, 548, 576, 583
Constam, Schläpfer, and Kolbe, 51
Cooper, 1189, 1201, 1614
Coppée, 88, 94, 95, 104, 105, 127, 154
Coppers, 1380
Corbin, 851
Cormack, 455
Cornu, 371
Cory, G. S., and Co., 546
Couffinhal, 546
Coulson, 368
Coupier, 922, 924, 926, 927, 947
Coutagne, 1110, 1113
Coutin, 851
Cox, 1258, 1260, 1266, 1268, 1337, 1338
Crafts, 944, 993
Craig, 397, 463, 1409, 1565
Craven and Coleman, 435
Crosby and Rigby, 1233
Crossley and Brighten, 1599
Crossley, Wheeler, and Smith, 393, 410
Crowther, 1548, 1550
Culmer, 361
Cunisset, 821
Cunningham, 1056
Cunow, 138
Curphey, 1384, 1522, 1614
Currie, 457, 590
Cusiter, 67
Custodis, Zerr, and Rübenkamp, 718
Cuyper, 1265
Cyanid-Gesellschaft m.b.H., 1055, 1124, 1128, 1130, 1132, 1133

Dach, 1600
Dafert and Miklauz, 1113
Dahl, 1487
Dahmen and Haggi Ristic, 373, 571
Daischner, 361
Dalston, 375
Dammann, 660
Danek, 596
Dankworth, 1123
Dannenberg, 98
Darmstädter, 1030
Daub, 938
Davidson, 82, 499, 942
Davies, 1303
Davies and Windsor-Richards, 371, 1598
Davis, 38, 67, 68, 69, 316, 348, 495, 497, 709, 732, 748, 844, 847, 862, 869, 948, 998, 1000, 1001, 1003, 1004, 1022, 1266, 1450, 1480, 1513
Davis and Lucas, 685
Davy, 1388, 1389
Dawes, 1113
Daguzan, 557
Dean and Downs, 519
Debus, 1306
Decher and Kopp, 905
Deck, 1321, 1480
Degener, 268, 800
Degrez and Cambier, 306
Dehne, 556
Dehnst, 831
Deichler, 655
Delaire, 251
De la Vergue Refrigerating Machine Co., 1395
Delbrück, 1305
Délépine, 1299
Délépine and Sornet, 1289
Dellwick and Fleischer, 180
Demady, 224
Dempster, 171, 175, 385, 1249, 1447, 1609
Denayrouze, 1020
Dengler, 215
Denigès, 985, 986
Dennis and M'Carthy, 85
Dennis and O'Neill, 85, 87
Dennstedt and Ahrens, 65, 241, 242, 282
Dennstedt, Hassler, and Bünz, 8
Dennstedt and Lehne, 305
Dennstedt and Voigtländer, 305
Dennstedt and Zimmermann, 294
Deussen, 1546
Deutsche Ammoniakwerke, 1167
Deutsche Ammoniak-Verkaufs-Vereinigung, 1572, 1612
Deutsche Benzolvereinigung, 1028, 1034
Deutsche Gas-Gesellschaft, 318, 386, 1015, 1327
Deutsche Gold- und Silber-Scheideanstalt, 1124, 1153, 1305, 1409
Deutsche Quarrit- und Bithulithic-Pflaster, G.m.b., 367, 558
Deutsche Teerprodukten Vereinigung, 674, 852, 1605
Deutsche Wassergas-Beleuchtungs-Gesellschaft, 1011
Devaucelles, 1123
Deville, 48, 64, 232, 235, 343, 673, 1031, 1091, 1301
Deville and Troost, 1301, 1303
Devinet, 1010
Dewar, 1292
Dewey, 719
Dexter, 344
Di Cosa, 800
Diamant-Brikettwerke, 1601

Diamond, 81, 1494
Dibbits, 1316
Dicke, 1609
Dickenson-Gair, 843
Dickinson, 504
Dieffenbach and Moldenhauer, 1060
Diehl, 1051
Diels and Bibergeil, 285
Diesel, 678
Dieterich, 1028
Dietrich, 1276
Dilette and Talabot, 1010
Dill, 1449
Dilla, 97
Dillon, 98
Dimroth, 228, 626, 986
Dingler's Maschinenfabrik, 1064, 1609
Dinsmore, 317, 318
Dioscorides, 1041, 1042, 1044
Dittmar, 41, 49
Ditz, 803, 804
Ditz and Cedivoda, 790, 802, 804, 805
Ditz and Clauser, 817
Divers, 1300, 1315, 1316, 1317, 1318, 1323, 1409, 1552, 1554, 1555
Divers and O'Haga, 1321
Divers and Ogawa, 1306
Döbner, 274, 299
Döbner and Miller, 298, 299
Doehring, 562
Doersch, 1380
Doherty, 1608
Donath, 72, 294, 763, 1153, 1612
Donath and Asriel, 308, 535
Donath and Ditz, 939
Donath and Frenzel, 1055, 1057, 1058
Donath and Margosches, 531, 586
Donati and Pollak, 1277
Donkin, 1091
Dorp, van, 256
Dörr, 360, 364
Dörr & Co., 360
Dossios, 443
Douglas, 79, 180, 573
Dovin and Hutton, 1043
Dow, 1255
Downs, 533
Downs and Deane, 16, 182, 183
Dowson, 813
Draiswerke, 875
Dralle, 1613
Drechsel, 1305
Dreher, 626
Drehschmidt, 52, 1185, 1191
Drew, 69
Drexler, 349
Dreyssig, 353
Drittler, 688
Dromain, 1177
Drory, 60
Dubosc and Henzey, 1330, 1534
Duckham, 97, 1593
Duden and Scharff, 1306
Duff, 1243
Duff and the Gas Power and By-products Co., 1232
Duggan, 1473
Duhamel, 1043
Dühring's Patentmaschinen-Gesellschaft, 836
Dumas, 18, 21, 1045, 1046, 1047, 1165
Dumas and Laurent, 250
Dumoulin and Coutelle, 665, 666
Duncan, 463, 1158
Dundonald, Lord, 18
Dunnachie, 1244
Duran, 1015
Durand-Claye, 585
Durand and Marais, 545
Dürkopf and Göttsch, 297
Dusart, 268
Duvieusart, 1195, 1483, 1536
Duyk, 820
Dvorkovich, 55, 193, 194
Dyes, 1569
Dynamite Aktien-Gesellschaft, 1087
Dyson, 1277, 1278, 1279, 1284, 1613
Dzwinowsky and Bachmann, 248
Dziewonski, 189

EASTERFIELD, 1484
Eastman, 1512
Ebell, 271, 769
Eckelt, 1448
Economic Gas and Coke Co., 98
Edison, 1605
Edlefoen, 244
Edler and Valenta, 1575
Effenberger, 1010
Effront, 1152
Eger, 796, 798, 804
Eggert, 1059
Egloff and Twomey, 1595
Egrot, 927
Ehmann, 574
Ehrhardt and Sehmer, 1226
Ehrlich and Graetz, 1096
Eichfelder and Winckelmann, 718
Einhorn and Gilbody, 295, 296
Eiseler, 361
Ekenberg, 1178
Elbs, 255, 1574
Elektrochemische Werke, Berlin, 1089, 1146, 1572
Ellean and Ennis, 1293
Ellerton, 939, 984, 988
Ellery, 317, 608, 646, 1471
Elliott, 181, 628
Ellis, 1111, 1450, 1609
Ellison and Davis, 426, 483
Elster, 845
Elyers and Pack, 1570

Emmert and Reingruber, 247
Endeman, 1067
Engelmann and Merkel, 1131
England, 813, 1484, 1488
Engler, 1, 2, 10, 131, 215, 236, 320, 335, 407, 423, 430, 526, 527, 552, 645, 713
Engler and Dieckhoff, 657, 817
Engler and Schneider, 217
English Home Office, 1036
English Mond Company, 1178
Ephraim, 1064, 1609
Ephraim and Pietrowsky, 1306
Epp, 547
Erckmann, 1317
Erdmann, 1052, 1294
Erlenbach, 1449, 1479
Erlenmeyer, 213, 245
Erlwein, 1140
Ernst, 1011, 1149, 1150
Ertel, 1114
Esop, 1549
Etard and Lambert, 66, 220, 221
Eulenburg, 1307
Evans and Mitchell, 1602
Everard, 545
Everitt, 56
Eyndhoven, van, 1502, 1606

Fabini, 768
Fabry, 1195, 1380
Fahlbusch, 766
Fairley, 1564, 1565
Falck, 878
Falls, 1466
Faraday, 26, 65, 187, 224, 225, 1300, 1308, 1388, 1389
Farbenfabriken Elberfeld vorm. Friedr. Bayer & Co., 616, 617, 810, 904, 1053, 1063, 1085, 1089, 1609
Farbwerke Höchst vorm. Meister, Lucius, and Brüning, 634, 904, 1048, 1216, 1572, 1607, 1608
Faxa, 353
Fayolle, 813
Feld, 60, 63, 138, 883, 1196, 1197, 1198, 1199, 1237, 1284, 1457, 1564, 1570
Feldmann, 1116, 1337, 1365, 1375, 1439, 1440, 1441, 1443, 1479
Fell, 1121
Felten, 560
Fenner, 419, 460
Fenner and Versmann, 567, 569, 570
Ferguson, 1297
Ferko, 223
Fernholz, 1020, 1021
Ferrand and Marsais, 539
Ferrari, 343
Festner and Hofmann, 98
Fichter and Brunner, 1611
Fichter and Oesterheld, 1110
Figuera, 1458
Fikentscher and Tromsdorff, 262
Fillunger, 1194, 1359
Filsinger, 605
Fiora, 272
Fischer, 92, 97, 255, 301, 351, 849, 980, 1152, 1266, 1606
Fischer and Koske, 794
Fischer, E. and O., 280
Fittig, 234, 249, 288
Fittig and Büchner, 249
Fittig and Ebert, 282
Fittig and Gebhardt, 258
Fittig and Hoogewerf, 278
Fittig and Ostermeyer, 256
Fleck, 1065, 1066
Fleischhauer, 59
Flückiger, 1308
Fogarty, 1119, 1120, 1252, 1512
Fohr and Kleinschmidt, 1600
Forbes and Abbott, 1498
Ford Motor Company, 61
Forel, 965
Forrest, 581, 704
Forst, 1478
Forster, 1185, 1255
Förster and Jacoby, 1125
Forster and Schmitz, 1185
Fortmann, 804, 845
Foster, 1188, 1222
Foucault, 390
Fouler, 1146
Fourcroy and Vauquelin, 1388
Fousset, 1457
Fowler, 1493
Fownes and Young, 1113
Francke, 1344, 1367, 1380, 1448, 1450, 1486, 1529
Frank, 155, 654, 688, 904, 965, 972, 978, 979, 980, 982, 989, 990, 1014, 1020, 1033, 1076, 1125, 1128, 1129, 1141, 1178, 1179, 1577
Frank and Caro, 1048, 1056, 1069, 1075, 1103, 1124, 1127, 1128, 1129, 1140, 1176, 1177, 1178, 1179, 1180, 1181, 1208, 1333
Frank, Caro, and Jacoby, 1140
Frank, Caro, and Linde, 1609
Frank and Fincke, 1112
Frank and Markwald, 1013
Frank, Pfleger, and Caro, 1103
Frank and Voigt, 1129, 1130
Frank, 1028
Frankland, 67, 209, 229, 1142
Frankland and Silvester, 1493
Frankland and Thorne, 229
Franklin, 1292
Franklin and Kraus, 1295, 1313
Franquoy, 539
Frasch, 893
Frauencron and Stack, 1240
Frederking, 454, 604

Freeth and Cocksedge, 1531, 1570
Frémy, 4
French, 1213, 1537
French Aluminium Syndicate, 1108
French Company Lesage, 1543
French Eastern Railways, 692
Frerichs, 1379, 1403, 1406, 1412, 1479
Frese, 295
Fresenius and Makin, 817
Fresnaye and Suchy, 1062
Freudenberg, 1124
Freyss, 1014
Friedel and Crafts, 234, 238, 267, 943, 998, 1606
Friedel and Pisani, 1051
Friedländer, 298, 664, 764, 811
Friedrich & Co., 560, 1537
Friedrich & Co. and Hirsch, 1536
Fries, 244
Friese, 354
Friswell, 4, 6, 941
Fritsch, 97
Fritzsche, 157, 158, 245, 250, 253, 254, 261, 262, 290, 809, 1480
Fronsac, 843
Froth, 1028
Fryklind, 1161
Fujiyama, 1133
Fuhst, 873
Fürbringer, 849
Fürth, 1194

GALLAND, 466
Gallup, 1573
Gans, 1299
Garden, 243
Gardner, 1396
Gareis, 1377
Garrett, 874
Garrett and Smythe, 293
Garroway, 1563, 1568
Gartsherrie, 171, 175, 179
Gas-Light and Coke Co., 81, 504
Gasch, 56, 1548
Gasmotorenfabrik Deutz, 60, 678, 848
Gasset, 370
Gassmann and Usines du Rhône, 822
Gaster, 395, 564
Gathmann, 883
Gattermann and Lockhart, 289
Gaultier de Claubry, 90
Gawalowski, 633, 975
Geber, 1043, 1044
General Chemical Co., 1089
General Reduction and By-products Co., 1609
de Gensanne, 17
Genthe, 844, 852
Gentles, 1533
Gentsch, 273, 810, 819
Gentzen, 360
Gerhard, 268
Gerhardt and Cahours, 236
Gerlach, 660, *1312, 1323, 1332, 1455, 1563*
Gerlach and Tieftrunck, *1257*
German *Ammonia-selling Union, 1486*
German *Coking Committee, 1515*
German *Exchequer Exports, 901*
German Federal Council, 902
German Imperial Board of Health, 807, 819
German Imperial Government, 1016
German Inland Revenue Office, 979
German Iron-founders' Union, 351
German Mond Gas Co., 1180
German Naval Office, 691
German Office of Telegraphs, 691
German Pharmacopœia, 792
German Railway Companies, 1405
German Society of Chemical Industry, 964
German Syndicate of Tar Product Manufacturers, 830, 840
German Union of Benzol Manufacturers, 952, 956
German Union for the Sale of Ammonia, 1289, 1517
Germania Engineering Works vorm. Schwalbe, 1396
Gerold and Vacherot, 1378
Gesellschaft für Abwasserklärung, 1160
Gesellschaft f. Linde's Eismaschinen, 1058
Gesellschaft für Teerverwertung, Duisburg-Meiderich, 162, 220, 241, 250, 302, 350, 626, 853, 905, 1605
Gesellschaft für Verwertung von Kohlenstoffverbindungen, 711
Geserich, 851
Gesner, 455
Gessert, 253
Gewerkschaft Deutscher Kaiser, 1028
Gewerkschaft König Ludwig, 79, 137
Gewerkschaft Lothringen and Uhde, 1569
Gewerkschaft Messel, 279
Gibbs, 767, 1292
Gill, 608, 1257
Gilly, 353
Gilmour, 1123
Girard and Delaire, 200, 388, 389, 407, 421, 442, 753, 755
Giraud, 372
Giulini Bros., 1111
Gladstone, 228, 1320
Glaser, 1556
Glaser and Bürstenbinder, 882
Glasgow, 97
Glashan, 443
Glauber, 1045, 1322
Glinzer, 1173
Glinzer and Fittig, 235
Glover, 158, 1067, 1601
Gmelin, 266
Gobiel, 95

Gobin, 557
Goethe, 18
Goldberg, 982
Goldberg and Siepermann, 1551
Goldschmidt 259
Goldschmidt and Constam, 291, 295
Goldschmidt and Schmidt, 252
Gordon, 271
Goriainoff, 1093
Görlich and Wichmann, 1147, 1551
Gorup-Besanez, 266
Gossler, 80
Gottbrecht, 1307
Gottesberg Coal & Coke Co., 119
Goulard, 718
Goulischambaroff, 676
Gouthière & Cie. and Ducancel, 1153
Grabowsky, 852
Graebe, 245, 249, 256, 257, 259, 268, 284, 301, 307
Graebe and Bungener, 260
Graebe and Caro, 280, 300
Graebe and Glaser, 306, 619
Graebe and Guye, 246
Graebe and Knecht, 307
Graebe and Liebermann, 21, 251, 253, 254, 450
Graebe, Liebermann, and Spiegel, 258
Graebe and Walter, 263
Graebe, 180, 225, 587, 975, 1011
Graf, 481
Graf & Co., 606
Gräf, 314
Graham, 603, 1057
Grahn, 1331
Graul, 1590
Gravenhorst, 1043, 1527
Graves, 1277
Gray, 275, 279
Grayson, 547
Grebel, 156, 317
Greening, 621
Greenstreet, 1611
Greiner, 338
Greville, 286
Griess, 267
Griffiths, 267
Groeck, 80
Groendal and Landin, 1565
Gröling, 495
Gröling and Estlander, 426
Gros, Goissedet, Bouchardy, and Fessier, 1118
Groschuff, 229
Gross, 256
Grossmann, 1068, 1257, 1334, 1335, 1450, 1453, 1454, 1494, 1495, 1496, 1547
Groth, 227
Grotowsky, 890
Grousilliers, 890
Grouven, 1169, 1212
Grove, 1301
Grube, 671
Grube and Krüger, 1137, 1611
Gruber, 274, 277
Grüneberg, 1337, 1347, 1378, 1432, 1439, 1440
Grüneberg and Blum, 1351, 1435, 1438
Gruner, 5
Grünewald, 289
Guardabassi and Goulliard, 1178
Guéguen and Parent, 1202
Guglielminetti and Schottelius, 362
Gui, 1611
Guignet, 4, 6, 308
Guillot and Brisset, 1177
Guissani, 657
Guiton de Morveau, 1388
Günther, 605
Gurlt, 17, 89, 91, 539
Gutensohn, 393
Gutknecht, 1333
Guttmann, 1563
Guttmann, Herzfeld, and Beer, 1014
Guye, 250
Guye and Picoza, 1291
Gwiggner, 63

HAACK, 850, 1122
Haarmann, 34, 65, 70, 115, 152, 155, 161, 163, 166
Haber, 86, 312, 1065, 1070, 1072, 1073, 1074, 1075, 1076, 1077, 1078, 1157, 1292, 1301, 1307
Haber and Greenwood, 1070, 1072
Haber and Maschke, 1303
Haber and Le Rossignol, 1070, 1071, 1074, 1076, 1291, 1400, 1612
Haber and Oechelhäuser, 86
Haber and van Oordt, 1071, 1303, 1304
Habets, 535
Hache, 373
Hadra, 808
Hager, 766, 787, 792
Hahn, 844
Haissig, 972
Haitinger, 293
Hake, 1163
Hall, 1595
Haller and Michel, 938
Halvorsen, 1612
Hamberg, 270
Hamilton, 175, 176, 417, 1246, 1251
Hammerl, 809
Hanekop, 1315
Hanekop and Reissmann, 1552
Hanks, 766
Hannemann and Boisly, 560
Hansel, 674
Hantzsch and Desch, 272
Hantzsch and Sebald, 1309
Harcke, 821

Hardin, 1389
Hardman, 68, 748
Hardman and Wischin, 602
Hargreaves, 348, 808
Haring, Ehrenberg, and Baswitz, 1150
Harker, 885
Harris and Weiss, 232
Hartenstein and Weber, 176
Hartley, Thomas, and Applebey, 295
Hartmann, 716, 1339, 1379, 1477
Hartmann and Luke, 666
Haskins, 374
Hasselt, 1307
Hatschek, 360
Hauenstein, 586
Hauff, 1123
Haupart and Carvès, 89
Hausenfelder, 641, 678
Häusler, 560
Hausman, 26[illegible]
Hausmann, 1008, 1608
Hausmann and Pilat, 193
Häussermann, 293, 303, 509, 755, 842, 899, 900, 935, 945, 947, 949, 955, 975
Hayes, 47
Heber, 1222, 1223
Heckert, 1089
Heckmann, 439, 934
Heeren, 1013
Hegener, 96, 1377
Heilpern and Haas, 360
Heinemann, 56, 1195, 1243
Heinrich, 851
Heinrici, 890
Heinz, 312
Heinzerling, 78, 679
Heise, 684
Helbig, 677
Helbing, 213
Helbing and Passmore, 807
Helch, 294
Helmers, 809
Helmont, 1044
Hélouis, 54
Hemingway, 1484, 1506
Hempel, 180, 317, 848, 1078, 1157, 1257, 1543, 1559
Hempel and Dennis, 85
Henderson, 171, 483, 1183, 1380
Hengst, Watson, Musehamp, and Wilson, 316
Henichke, 813
Hennebutte and Vauréal, 1458
Hennin, 1190, 1212
Henriques, 1183
Henry, 1273, 1304, 157[illegible]
Henz, 137
Hepworth, 1320, 1337, 1338
Herberts, 96
Herborn, 606
Herbst, 161, 1322
Herford, 1094
Herr, 959
Herre, 1110
Herring, 546, 1589
Herry, 1334
Herting, 1270, 1279, 1280
Hertkorn, 1315
Herwegen, 5, 96
Herzfeld and Beer, 1014, 1016
Herzog, 273, 804
Heskin, 1536
Heusler, 41, 215, 217, 239, 265, 305, 312, 510, 894, 938, 1183
Heusler and Herde, 641
Heuss, 78, 141, 1449, 1474, 1475, 1497
Heusser, 55, 335, 554
Heyden, 341, 1020
Heyden's Nachfolger, 809
Heyden and The General Electric Co., 1096
Heydenreich and Beilstein, 812
Heys, 1123
Higgins and Preston, 1028
Hilgenstock, 98, 114, 137, 1192, 1237, 1244, 1245, 1358, 1528, 1557, 1588, 1614. *See also* Otto-Hilgenstock
Hill, 1450, 1600
Hilleke, 1480, 1612
Hills, 1378, 1465
Hilpert, 1596, 1606
Hiltawski and Kahnert, 96
Hiltner, 607
Hinrichsen, 1544
Hinselmann, 1195, 1486, 1530, 1539, 1572
Hippocrates, 1042
Hirn, 263
Hirsch, 475, 838
Hirschsohn, 807
Hirth, 1403
Hirzel, 72, 74, 75, 185, 227, 359, 490, 491, 881, 1374, 1375, 1380, 1443, 1446, 1450, 1589, 1593
Hiscott, 807
Hisinger and Berzelius, 1308
Hislop, 1212
Hlawaty, 191, 1088, 1573, 1609, 1619
Hobbs, 1597
Hoddick and Röthe, 1599
Hodgkinson and Mathews, 250, 285
Hodurek, 308, 524, 576, 583, 605, 606, 607, 646
Hoepfner, 360
Hoffmann, 96, 105, 117, 151, 417, 712, 1010
Hoffmann-Otto. *See* Otto
Hofmann, 1010
Hofman, A. W., 20, 225, 226, 293, 940, 982, 1187, 1301, 1304, 1308
Hofmann, P. W., 767
Hohenhausen, 868, 918, 927, 950, 954
Holde, 228, 556, 901, 975

Holden, 339
Holgate, 1380, 1450, 1456
Holland, 636
Holland and Phillips, 981
Holliday, 1018
Holmes, 56, 577, 578, 1512
Holmes and Howell, 1450
Holtz, 812
Homann, 606
Homburg, 812
Homer, 1606
Hönigsberger, 34, 1019, 1028
Hönigschmidt, 1611
Hood and Salamon, 1551
Hoogewerp and van Dorp, 299
Hooker, 305
Hooper, 153, 525, 1093
Hoppe-Seyler, 3, 267
Horn, 328, 339
Hörnig, 96
Houghton, 1289
Houzeau and Renard, 232
Howard and Morse, 581
Hubbard, 153
Huber and Poindexter, 1152
Hübner, 185, 738, 872, 873
Hübsch, 607
Hüdec, 1149
Hughes, 97
Hulwa, 82[illegible]
Humphreys and Glasgow, 180
Hunt and Mirck, 349
Hunter, 1300
Huntingdon, 1098
d'Hurcourt, 1046
Hurford, 1056
Hüssener, 72, 79, 89, 92, 96, 98, 119, 127, 131, 135, 823
Hutchinson, 96, 101, 552
Hüttemann and Spieker, 546
Hutton Company, 848

IHLDEN, 295
Ilges, 495
Illingworth, 1499
Imperial Continental Gas Association, 511
Imray, 173, 1251
Indre and Thierry, 1152
Industrie Gesellschaft für Sauerstoff und Stickstoffanlagen, 1608
International Agricultural Corporation, 1152
Internationale Wasserstoff Aktien-Gesellschaft, 1063
Ipatieff, 314
Ireland and Fugden, 1176
Irinyi, 678, 849
Irvine, 628, 716
Irvine and Mitchell, 719
Irwin, 1022
Irwin, 987
Isambert, 1338
Isleib, 1545
Isoard, 316

JACK, 367
Jackson, 341
Jackson and White, 251, 257
Jacobi, 873
Jacobius & Sons, 359
Jacobs, 226
Jocobsen, 210, 234, 235, 236, 237, 310, 311, 313, 394, 920, 993
Jacobsen and Reimer, 299
Jahn, 558, 1070, 1089, 1090
Jaloureau, 561
James, 1607
Jameson, 96, 99, 100, 101, 106
Jane, Elland, and Steuart, 749
Japp and Schultz, 255
Jaubert, 1058
Jayne, 153, 519, 520
Jean & Cie., 1161, 1379, 1449
Jellinek, 1087
Jenker, 546
Jenkins, 87
Jenny, 888
Jevons, 1610
Jeyes, 658, 808
Jicinsky, 1190
Joecks, 360
Johnson, 983, 987, 1061, 1067, 1068, 1079, 1138, 1144, 1145, 1484, 1567
Jolicard, 1587
Jones, 89, 90, 170
Jones and Suarez, 1177
Jonescu, 813
Jordan, 1043
Jorrissen and Rutten, 843
Josse, 674, 676
Julius Pintsch Aktien-Gesellschaft, 1062, 1394
Jünemann, 539
Jung and Must, 873

KAG, 353
Kahlenberg, 904
Kaiser, 1102, 1113, 1333
Kämpf, 343
Kane, 237
Kapert, 360
Kassner, 1608
Kastner, 118
Kaufman, 335
Kausch, 1061, 1608
Kay-Thompson, Gonzalez, and Blake, 1137
Kayser, 349
Kehlstadt, 290

Keiler, 816
Keillor, 1448
Kekulé, 228, 268
Kéler, 1103
Kelhöfer, 806
Keller, 9
Kellner, 821, 1147
Kelly and Weigel, 1332
Kendal, 82, 83
Kennedy, 1471
Kent, 503
Kenyon, 709, 1203, 1213
Keppich, 1380
Keppler, 802
Kerl-Stohmann, 39
Kerner, 1157
Kerpely, 1225
Kestner, 1457
Ketjen, 1156
Kewener, 1609
Key, 328
Kipping, 261
Kirchhoff, 1611
Kissel, 407, 468
Kitt, 288
Kitson & Co., 847
Kjeldahl, 642, 1143, 1165
Klages, 240
Klar, 185
Klaudy and Finck, 264
Kleeberg, 813
Kleinert, 789, 801
Kleist, 98
Klepl, 268
Kletzinsky, 821
Klimont, 579
Klisch, 793
Klocke, 431, 1011
Klönne, 96, 102, 386, 392
Klotz, 1388
Kloz, 260
Klutt, 1146
Knab, 89, 90, 91, 119, 481, 1200, 1570
Knab-Carvès, 90, 99
Kniess, 1012
Knights and Gall, 735, 746
Knoedler, 1406
Knoll & Co., 606, 661, 664, 814
Knop, 1274, 1305
Knorr, 299, 1309
Knorre, 1575
Knowles, 1608, 1609
Knublauch, 65, 229, 1022, 1167, 1185, 1188, 1191, 1202, 1269
Koch, 371
Koch, Wolfhügel, and Knorre, 271
Kochendörfer, 1612
Koechlin, Duchatel, and Perpigna, 316
Koehn, 341
Koelsch, 1611
Koepp & Co., 1064
Köhler, 19, 32, 34, 70, 156, 219, 252, 266, 291, 308, 311, 314, 353, 380, 383, 406, 418, 438, 442, 452, 479, 522, 523, 581, 586, 588, 602, 678, 712, 714, 719, 723, 745, 746, 748, 749, 812, 831, 850, 851, 891, 1027, 1392
Kohlrepp and Wohl, 1205
Kohn, 631, 769
Kohn-Abrest, 1110
Kohn and Friger, 768
Köhn, 491
Köhn and Münster, 393
Kolbe, 581
Kolbe and Schmitt, 280
Kölner Russfabriken, 716
Kölnische Maschinenbau Aktien-Gesellschaft, 180
Kompa, 282
König, 240, 1492
Konowalow, 216, 443, 1299
Konowalow and Markownikow, 216
Kopp, 225, 227, 228, 269, 453, 454, 571, 633, 744, 1041, 1042, 1043, 1044
Koppers, 60, 138, 876, 913, 1090, 1139, 1194, 1207, 1232, 1236, 1237, 1253, 1449, 1477, 1486, 1487, 1592
Koppeschaar, 787, 789, 798, 799, 800, 801, 802, 805, 818
Kordt, 1380
Korn, 802
Korter, 1237
Körting, 348, 378, 1329
Körting Brothers, 62, 338, 349, 1249
Kosmann, 541
Kovács, 581
Kraemer, 27, 50, 65, 67, 70, 155, 201, 237, 252, 257, 261, 262, 264, 265, 274, 297, 304, 308, 311, 312, 318, 348, 389, 396, 399, 467, 475, 477, 498, 500, 516, 523, 532, 554, 573, 616, 707, 709, 747, 767, 830, 937, 945, 1016, 1019, 1028, 1032
Kraemer and Böttcher, 215, 235, 236, 246
Kraemer and Sarnow, 580, 581
Kraemer and Spilker, 67, 219, 221, 228, 232, 239, 240, 242, 246, 251, 252, 256, 257, 261, 271, 282, 283, 284, 300, 306, 309, 519, 524, 525, 576, 600, 616, 626, 641, 643, 664, 703, 733, 735, 744, 794, 855, 856, 864, 870, 875, 897, 947, 950, 951, 952, 965, 972, 978, 979, 982
Kraemer, Spilker, Eberhardt, and Klotz, 312
Kraemer and Weissgerber, 284, 285, 289, 645
Krafft and Weylandt, 253
Kramers, 314
Krauch, 1388
Kraus, 7, 262
Krauss, 1134
Krauss, Kappen, and Aktien-Gesellschaft f. Stickstoffdünger, 1611

Krauss, Stähelin und Aktien-Gesellschaft f. Stickstoffdünger, 1134
Kraut, 1305, 1313
Krayenbühl, Peterson, and Burmeister, 386
Krebs, 1403
Kreis, 852, 985, 989
Kremel, 271
Kremer, 1359
Kresz, 1380
Kretzschmar, 690, 891
Krausel, 766
Krey, 466
Krickhuhn, 1599
Kridlo, 571
Krieger, 87
Krojanker, 689, 1015
Krömer, 237
Kronstein, 240
Kropff, 439, 1613
Kros, 137
Kubel, 812
Kubierschky, 458, 459, 494, 935, 458
Kuentz, 1156, 1532
Kues and Paal, 288
Kühling and Berkold, 1125
Kuhlmann, 349, 1332
Kuhn, 519
Kühne and Bredig, 1611
Kunath, 55, 385
Kunheim & Co., 1064, 1087, 1455, 1556, 1559
Kunkel, 1044
Künkler, 660
Kunow, 80
Kuntze, 1170
Kunz, 626
Künzel, 1386
Kupfferschläger, 1385
Kuriloff, 1300
Kusch, 877
Kusch, Teubner, and Deutsche Erdölwerke, 406
Küster, 842
Kützbach, 678
Kyan, 679

LA BELLE Iron Works, 159
Ladenburg, 296, 737
Lagrange, 1579
Lainer, 975
Lair, 1458
de Laire, 814
Lamb, 704, 1123, 1136
Lambilly, 1120
Laming, 1238, 1480
Lance and Elworthy, 1123
Landis, 1135, 1138, 1611
Landmark, 1099
Landolt, 267, 798
Landolt and Baumert, 1305
Landshoff and Meyer, 737
Lange, 1292, 1293, 1405, 1408
Lange and Hertz, 1408, 1411
Lange and Heffter, 1410
Langlands and O'Connor, 1476
Langloan, 171, 175
Langlois, 1305
Laser, 810
Laubenheimer, 286, 288, 289, 984
Laurent, 243, 244, 256, 259, 260, 266, 731, 732, 737
Lavaux, 256
Layman & Co., 1484
La Wall and Fullerton, 808
Leahy, 627
Leaver, 368
Lebel-Henninger, 994
Le Blanc, 1094
Le Blanc and Eckhardt, 1576
Lebon, 18, 352
Le Chatelier and Bogitch, 1570
Le Clercq's Patent Gesellschaft, 439
Lederer and Gintl, 1150
Ledig, 1475
Leede and Ouray, 327
Leeds, 232, 267
Legge, 574
Legrand and Dabernard, 1150
Lehmann, 254, 509, 793, 1307, 1385
Lehmbeck, 1028
Leigh, 82, 225, 376
Lelarge, 1587
Lembach and Schleicher, 809
Léméry, 1043, 1044
Lemmer, 393
Lemmert, 495
Lemoine, 531, 532
Le Morvan, 1609
Lencauchez, 1169, 1460, 1461
Lendert, 968, 990
Lengholz, 711
Lenk and Lehmann, 546
Lennard, 395, 460, 473, 483, 484, 485, 1559
Lennox, 1565
Lenz, 329, 331, 332
Leo, 583, 1515
Lepsius, 1094, 1199
Le Ray, 548
Lesage, 1564
Leschhorn, 98
Lesher, 1591
Lesimple, 284
Lespican, 263
Lessing, 553, 1244
Lessing and Wilton, 900, 1507
Letheby, 503, 504, 928, 1022
Letny, 188, 189
Leube, 802
Levin, 1609
Levinstein, 70, 105, 236, 605, 945, 992, 993, 1030

Levy, 289
Lewes, 46, 182, 187, 194, 312, 313
Lewin, 230
Lewis, 346, 1556
Lewis and Adams, 1614
Leybold, 317, 1269
L'Hôte, 1165
Libavius, 1045
Liddle and Barnes, 1279
Lidholm, 1102, 1132
Lidholm and Dettifoss Powder Co., 1131, 1611
Liebau, 688
Lieben, 267
Liebermann, 189, 190, 260, 272, 287, 586, 984
Liebermann and Bergami, 261
Liebermann and Burg, 188
Liebermann and Peur, 984, 985
Liebermann and Seyewetz, 936, 980, 983
Liebermann and Spiegel, 250, 261, 262, 263
Liebig, 224, 697, 1046
Liegel, 325
Lilienfeld, 1609
Limpricht, 251, 285
Linde, 1047, 1058
Linde Ice-machine Company, 1411
Linder, 1258, 1259, 1260, 1264, 1279, 1282, 1284, 1515
Lindner, 719
Link, 830
Linton, 323
Lippmann, 1041, 1042
Lippmann and Pollak, 938
Lipski, 1087, 1112, 1125
Lipszyc, 919
Lister, 821
Litchfield and Renshaw, 327
Little, 848
Livesey, 342, 1599
Livesey and Kidd, 824, 845
Ljnbawin, 293
Lloyd, 801, 1195, 1517
Lobb, 1506
Lobry de Bruyn, 1323
Lodge, 718
Loeb, 228, 626
Loebell, 587
Loew, 1053, 1145
Löhnes, 1127
Loir and Dryon, 1292, 1295, 1307
Longstaffe, 375
Loof, 293
Lorenz, 1254
Lorenzen, 1164
Lothringer Eisenwerke, 97
Loud, 1602
Louguinine, 233, 234
Löw-Beer, 485
Lowe, 180, 182, 732, 733, 734, 756, 760, 762, 787, 788, 791, 794
Lowe and Gill, 745, 762, 763
Lowry and Bernhard, 396
Lubawin, 304
Lubberger, 1269, 1491
Lübecker Apparatebau-Gesellschaft, 491
Lübke, 1015
Lucas, 255, 602
Lucion and Paepe, 1412
Luck, 594, 614, 627, 633, 634
Lück, 359
Lückau, 354
Lüdecke, 1052
Ludowici, 711
Luft, 813
Luhmann, 354, 438, 716
Lührig, 910
Lukin, 681
Lumina, 1137
Lunge, 189, 410, 503, 513, 520, 550, 586, 588, 609, 612, 620, 746, 747, 784, 830, 870, 884, 886, 893, 949, 960, 963, 999, 1000, 1004, 1016, 1053, 1075, 1103, 1145, 1147, 1166, 1254, 1268, 1270, 1276, 1283, 1318; 1341, 1358, 1424, 1426, 1464, 1465, 1466, 1467, 1469, 1488, 1503, 1519, 1545, 1559, 1573, 1577
Lunge and Harbeck, 86
Lunge and von Kéler, 83
Lunge and Köhler, 80, 1041, 1392, 1443, 1450
Lunge and Krepelka, 586
Lunge and Mohler, 297
Lunge and Rosenberg, 296
Lunge and J. Schmid, 148
Lunge and Smith, 1053, 1145, 1147
Lunge and Steinkauler, 250
Lunge and Wiernik, 1297
Lunge and Zschokke, 277, 784, 788, 795, 796
Lupton, 244
Lürmann, 96, 98, 104
Luther and Rose, 672
Luther and Weigert, 254
Lutze, 813
Lux, 60
Luyten and Blumer, 617
Lyle and Hannay, 668
Lymn, 1178, 1180, 1195, 1223, 1225, 1226, 1227, 1228, 1232, 1253
Lyndall and Castley-White, 1010
Lyons and Broadwell, 1095
Lyte, 1066

MABERY, 234
Mabery and Sieplein, 580
Macadam, 186
MacArthur, 808
M'Court and Ellis, 1611
M'Cracken, Newton, Kirkland, and Hussen, 316
M'Culloch and Reid, 97

M'Dougall, 371, 812, 1238, 1330, 1480
Mackay, 173, 1251
Mackay and Hutcheson, 1121
M'Kee, 226
Mackenzie, 295, 905, 1483
Mackintosh, 20, 375, 1012
Maclaurin, 1203
M'Murtrie, 675
Macquer-Leonhardi, 224
Maechtolf, 716
Maercker, 821, 1516
Mahon, 1134
Main and Galbraith, 171, 176, 1248
Malatesta and Germain, 903
Malden, W. J. and A., 539
Malenkowic, 555, 586
Mallet, 481, 1057, 1337, 1375, 1400, 1427, 1432, 1441, 1446, 1458
Mallet and Pagniez, 1377
Mallet and Payet, 363
Mallmann, 153, 264, 825
Malo, 585
Mann, 372, 563
Männel, 676
Mannesmann, 1404, 1405
Mansfield, 20, 26, 225, 227, 229, 232, 236, 290, 376, 866, 880, 922
Maquenne, 215, 216
Marasse, 268, 278, 1548
Marchand, 1319
Marchisis and Stevens, 554
Marcusson, 1601
Marcusson and Eickmann, 555
Maréchal, 1379
Margirino, 98
Margis, 1057
Margoles, 1112
Margosches, 231, 581
Margueritte and Sourdeval, 1114, 1115, 1458
Markgraf, 1204
Markl, 341, 498, 573
Markownikoff, 215, 219, 222, 225, 236, 246
Markownikoff and Oglobin, 267
Markownikoff and Spady, 210
Marr, 1380
Marriott, 370, 1167, 1473
Mars, Buqua, and Laurette, 1243
Marsay, 540
Marshall, 1574
Martellière, 1330
Martin, 98
Martini and Hüncke, 1009
Marum, 1388
Marzell, 753, 762
Mascarelli, 801
Maschinenbau-Anstalt Humboldt, 1062
Maschinenfabrik Augsburg-Nürnberg, 678
Maschinenfabrik Fürth, 1395, 1396, 1399, 1404, 1406, 1609
Mason, 487, 748
Mason's Power Co., 1232
Massol, 1203
Mather, 1450
Mathews and Goulden, 182
Mathies & Co., 361
Mathiessen, 1151
Matignon, 1087, 1090, 1110
Matignon and Lassieur, 1101
Matsumoto, 814
Matthieson and Hawliczek, 1147
Matthiesson, 1161
Maxwell, 408
Mayer, Adolf, 679
Mayer, M., 825
Mayer and Altmayer, 1198
Mayer and Hempel, 1264, 1283, 1284
Maywald, 523
Mazeline, 545, 546
Mazza, 1057
Meadows, 1466
Meffert, 193
Mehner, 1112, 1121
Meikle, 495
Meiser, 718
Meister, Lucius, and Brüning, 634
Melamid and Grötzinger, 498, 656, 710, 857
Mellor, 65
Mendelejeff, 227, 965
Menge, 1570
Mennecke, 889, 1014
Menzel, 386
Menzel Söhne, 1339, 1379
Merck, 904
Merkens, 317, 341
Merrill, 369
Messerschmidt, 1023, 1061, 1609
Messinger, 288
Messinger and Vortmann, 802, 1285
Mettler, 1608
Meunier, 228
Meurez, 722
Mewes, 1608
Meyer, Emil, 1150
Meyer, E. von, 9
Meyer, Th., 1579
Meyer, V., 231, 286, 304, 880, 984
Meyer, V., and Calm, 287
Meyer, V., and Kreis, 288
Meyer, V., and Sandmeyer, 287
Meyke, 271, 766
Michel, 894
Middleton and Detombay, 545
Milbauer and Stanek, 901
Milburn, 1513
Milde, 1111
Millar (George) & Co., 462
Miller, 934
Mills, 16, 201, 309, 362, 548, 583, 746, 831, 1546
Milne, 1272

Minimax Co., Ltd., 885
Miolati, 1576
Misteli, 87
Mitscherlich, 224, 227, 375
Mittasch, 1078
Mittasch and Morawitz, 1482
Mittasch and Schneider, 1059, 1609
Mix, 1596
Moehlau and Berger, 247
Moerk, 801
Moerman-Laubuhr, 1115
Mohr, 1028
Moissan, 1125, 1295
Mott, 680, 681
Mollier, 1296, 1298
Molz, 607
Monari and Scoccianti, 293
Mond, 167, 168, 174, 1066, 1067, 1095, 1115, 1118, 1167, 1213, 1214, 1217, 1218, 1221, 1222, 1233, 1252
Mond Gas Corporation, 1181
Monier, 316
Monthey, 261
Montmagnon and Delaire, 1057
Moon, 158
Moore, 48, 1449, 1597
Moore and the Dowson and Mason Gas Plant Co., 169, 1253
Morrell and Burgen, 1610
Morris, 1403
Morrison, 1608
Mörth, 328, 341
Morton, 85, 86
Moschner, 238, 242, 626
Muck, 4, 5, 6, 7, 576, 578
Mueller, 244, 718, 812
Muhé, 1458
Muir, 1403
Müller, 87, 388, 396, 553, 678, 732, 770, 849, 1190, 1488, 1611
Müller and Geisenberger, 1091
Münd, 1009
Munk, 267
Müntz and Girard, 1177
Murdoch, 18
Muter, 792, 803
Muter and de Koninck, 818
Muth, 1582
Mylius, 766, 1463

NAEF, 1342, 1380, 1545
Nagy, 688, 1305
Näher and Nöding, 1059, 1609
Namias, 1575
Natterer, 1389
Naumann, 227, 234, 443, 444, 1517, 1531, 1567
Naylor, 1166
Nebeling, 360
Neilson, 171, 176, 1246
Neilson and Snodgrass, 1183
Neimke, 1051
Nencki, 280
Neoghi and Adhicari, 1078, 1561
Nepp, 715
Nernst, 1065, 1160, 1291
Nernst and Jost, 1303
Neubäcker, 439
Neubeck, 1590
Neue Augsburger Kattunfabrik, 822
Neujean, 835
Neuhaus and Henniges, 546
Neumann, 224, 1028, 1058, 1599
Neumayer, 1475
Neumeyer, 1254
Neuninger, 718
Newson, 716, 1114
Ney, 765, 1605
Nicholson, 96
Nickels, 637, 640, 970, 971, 982
Nicol, 640
Nienhaus, 918
Nietsch, 802
Nikiforow, 191, 192, 193, 395
Nithack, 1091, 1123, 1572
Nitrogen Company, Ossining, 1135, 1608
Nitrogen-Gesellschaft m.b.H., 1055, 1608
Nitrogen Products Co., 1101, 1140
Nobbe and Richter, 1029
Nobel, 189, 190, 329, 332, 336, 338, 709
Nodon, 1612
Noll, 1146
Nölting, 279, 306
Nölting and Palmer, 237
Nölting, Witt, and Forel, 993
Nördlinger, 607, 645, 662, 664, 712, 810
Norsk Hydro-Elektrisk-Kvaelstof-Aktieselskab, 1562, 1568, 1569
North-Western Cyanamide Co., 1135, 1136
Northall-Laurie, 993
Northern Quarries Co., 366, 558
Norton and Noyes, 223
Nöthling, 556
Nouvelle, 1531
Nowicki, 87, 967
Nurnberg Consortium für chemische Industrie, 1575
Nydegger and Wedekind, 1569

OBERSCHLESISCHE Kokswerke, 1612
Oechelhäuser, 89
Oehler, 292, 1011
Oesterr. Verein für chemische und metallurgische Produktion, 1139
Ogilvie, 716
Oglobine, 192
Oldham Corporation, 1589
Olivier, 801
O'Neill, 32
Opitz and Klotz, 454
Oppenheimer and Kent, 394
O'Reilly, 396

Orlow, 272
Ormandy, Walker, and Holroyd, 1383
Orndorf and Cameron, 255
Ortmann, 659
Orvis, 327
Osius, 1449
Ost, 1152, 1386
Ostreijka, 439
Ostwald, 1049, 1333, 1572
Ott, 52, 60, 682, 1192
Öttner, 386
Otto, 98, 105, 110, 198, 359, 946, 1236
Otto and Beckurts, 658, 659
Otto & Co. (Dr C.), 61, 80, 92, 93, 96, 97, 98, 103, 105, 111, 114, 116, 137, 138, 141, 157, 163, 178, 1195, 1242, 1244, 1335, 1379, 1478, 1537, 1591, 1592
Otto-Hilgenstock, 111, 113, 115, 117
Otto and Lürmann, 97
Otto-Hoffmann, 105, 111, 154
Otto-Coke and Chemical Company, 111
Outon, 1448

PAAL and Puschel, 289
Pagliani and Ems, 1300
Pallenberg, 1479
Pampe, 1380
Paradill-Mateu, 827
Paradis, 352
Paris Automnibus Company, 1028
Paris Gas Company, 51, 64, 707, 709
Parker and Robinson, 1548
Pataky, 1151
Patent Block-tar, Motor-oil, and Asphalt Co., 370
Paternò and Fileti, 251
Patrouilleau, 1611
Patten and Robinson, 1046
Pattinson, 845
Paul Meyer Aktien-Gesellschaft, 552
Pauli, 1147
Pauling, 1585
Pauwels, 40, 146
Pauwels-Dubochet, 89, 99, 189
Payen, 537
Payne, 522
Payne and Clarke, 573
Peacock, 1085, 1102, 1112, 1113, 1122, 1132, 1134, 1135, 1137, 1148, 1239
Pearson, 658, 1602
Pebal and Freund, 267
Peceker Zuckerraffinerie, 1152
Péchiney & Co., 1342
Peck, 370
Pelletier and Walter, 232, 236, 262
Pelouze, 229, 849
Pelouze and Audouin, 58, 60, 61, 114, 138, 144, 183
Pelouze and Cahours, 214
Pelton, 682, 683
Peniakoff, 1112
Pennock, 361
Pennock and Morton, 1384, 1386
Pensky, 645
Perkin, 20, 21, 26, 211, 612, 618, 620, 628, 629, 632, 637, 640, 1181, 1182
Perkin and Hodgkinson, 251
Perkin and Revay, 241
Perlewitz, 852
Perman, 1298
Perman and Atkinson, 1303
Perman and Davies, 1291
Pernolet, 91, 102, 119
Perret, 623, 1499
Persoz, 280
Peters, 51, 272, 1236, 1339, 1477, 1575
Petersen, 983
Peterson-Kinberg, 354, 359, 441, 473, 501, 560
Pettenkofer, 812, 1307
Pfannenschmidt, 1331
Pfeiffer, 86, 87, 1284, 1361, 1362, 1387, 1388, 1551
Pfister, 1010
Pfleger, 1305
Pfrenger, 817
Philip, 847
Phillips, 1088
Phipson, 1548
Phœnix Aktien-Gesellschaft, 894, 1607
Picák, 138
Pick, 672, 673
Pictet, 1058, 1062, 1390
Pictet and Bouvier, 48, 218
Pictet and Ramseyer, 7
Pieper, 1172, 1231
Pier, 1064, 1079, 1082, 1090, 1600
Pietrusky, 80, 194, 675, 677
Pinchbeck, 1286
Pintsch, 1443
Pintsch, Julius, Aktien-Gesellschaft, 180, 185, 1358, 1365, 1473, 1609
Place, 1608
Planes, Ltd., and Thompson, 710
Planner, 850
Planting, 56
Planitz, 1569
Plate and Lieb, 547
Playfair, 1183
Playfair and Wanklyn, 1296
Plehn, 921, 1020
Pliny, 1041, 1042, 1044
van der Ploeg, 664
Plzak, 1478
Poetter & Co., 137
Poillon, 390
Pölecke, 1149
Pollacci, 1125, 1126
Pollard, 1463
Pont de Nemours Powder Co., 1102, 1573
Potter and Ovitz, 92
Possoz and Boissière, 1114

Potonié, 2
Pott, 1194
Powell, 367, 558
Power Gas Corporation, 1227
Pranke, 1611
Preissig, 539
Price, 1205
Propfe, 488, 498
Proschwitzky, 1166
Prussian Railroad Management, 703
Prussian Ministry for Agriculture, 1137
Pryce, 186
Pschorr, 257, 258
Puls, 564
Püning, 61, 157, 1205
Purves, 62, 499, 1336

QUAGLIO, 97
Quantin, 1386

RAAB, 300
Rabe, 257
Radcliffe, 1495
Radzizewski and Wispek, [illegible]93
Raetz, 813
Ragosine, 193
Ragosine and Dworkowitsch, 891
Raikow, 228
Raikow and Uerkewitch, 992
Rambousek, 230, 288, 314, 435
Ramdohr, 738
Ramsay, 293
Ramsay and Young, 1068, 1078, 1253, 1301, 1303
Raoult, 1299, 1301, 1323
Rapp, 661, 819
Rasch, 1011
Raschen and Brock, 1147
Raschig, 272, 273, 275, 292, 361, 367, 495, 803, 804, 805, 807, 823, 1602, 1603, 1604, 1605
Rasenack, 262
Raspe, 1557
Rassow, 1141
Rau, 8, 11, 52, 54, 155, 948, 1022, 1027, 1048, 1202, 1236, 1237, 1573
Raupenstrauch, 808
Rave, 889
Ray, 493
Raymundus Lullus, 1044
Readman, 1121
Redman, Weith, and Brock, 801
Redwood, 190, 191, 329, 336, 1164, 1182, 1183, 1189
Reformatzki, 216
Regnault, 227, 475, 958, 1091, 1292, 1293
Regnault and Forcrand, 1292
Rehländer, 243
Reichenbach, 266
Reichhardt and Bueb, 1153
Reichmann, 494
Reik, 1319, 1325
Reilly, 353
Reineke, 87, 1590
Reingruber, 246
Reinhardt, 1505
Reininger, 1243
Reinsch, 7
Reissert, 253
Reissmann, 1315
Remy, 98, 151
Renard, 215, 289
Reuss, 660, 817
Reuter, 271, 803, 943, 944, 993
Revollier, 546
Reyhe and Söhne, 812
Rhodes and Glossop, 368
Richard, 360
Richards and Shipley, 227
Richardson, 271, 323, 768, 1412
Richter, 885
Richters, 1166, 1206
Richters and Hagen, 1159
Rickman, 1066
Rickman and Thompson, 1067, 1158
Riedel, 300, 301, 810, 1055
Rieppel, 673, 678
Ries, 1022, 1162
Riesenfeld, 791
Rigby, 137, 1252
Rigby and Wet-Carbonizing Ltd., 1127, 1182, 1252, 1487, 1612
Riley, 174, 558, 559
Rincker and Wolter, 319
Rispler, 153, 329, 378, 393, 399, 400, 409, 423, 426, 460, 479, 500, 501, 511, 512, 519, 523, 590, 593, 594, 613, 614, 6[illegible]0, 653, 654, 675, 726, 728, 825, 827, 829, 839, 855
Ritthausen, 234
Rittman, 1[illegible]4, 1594
Rittmann and Egloff, 1595
Rives, 352
Robbins, 352
Robert and Irinyi, 1600
Robertson, H. S., 547
Robinson, 201, 470, 499, 575
Robinson and Goodwin, 302
Robiquet and Colin, 260
Röchling, 97
Rockwell & Co., 677
Roedelius, 360
Roelofsen, 1195
Rohart, 654
Rolla, [illegible]125
Rollason, 1588, 1589
Rolle, 873
Römer and Link, 635
Rommier, 238
Ronalds, 49, 50
Ronalds and Richardson, 881
Roos, 793

Röpert, 608
Roscoe, 220, 221, 375, 505
Roscoe and Dittmar, 1296
Rosemann, 661, 808
Rosenfeld, 1304
Rosenkranz, 1475
Rosenthal, 265, 266, 268, 279, 293, 1009
Rösing, 718
Rossel and Franck, 1100
Rossi, 1181
Rössler, 891
Rössler and Reinhard, 718
Roth, 554, 1057, 1058, 1086, 1096, 1103, 1564
Rothe, 1064, 1124, 1146, 1609
Rothermund, 1299, 1477
Rothberg, 111
Rougeot, 583
Rousseau, 1377
Roustan, 1512
Rowan, 1221, 1253
Rowlands, 1167
Royal Commission on Sewage, 1494
Rube, Engelcke, and Kraus, 1377
Rubitschung, 360, 364
Rudeloff, 1563
Rüderer, Loé, and Gumbart, 1170
Rudnew, 189
Rudolfi, 1125
Ruff and Treidel, 1100
Ruffi, 289
Runge, 266, 280, 281, 291, 299, 304, 722, 1608
Rüping, 664, 686
Rupert, 1298
Ruppert, 96, 119, 386
Rusby, 97
Rusch, 560
Russig, 31, 32, 33, 137, 274, 284, 313, 314, 576, 581, 583, 588, 622, 629, 721, 819, 939, 1014, 1030
Russig and Fortmann, 804, 805
Rütgers, 27, 369, 685, 686, 813
Rütgerswerke Aktien-Gesellschaft, 390, 396, 564, 605, 655, 656, 657, 686, 717, 835, 849, 850, 852, 1028, 1599
Rütgerswerke Aktien-Gesellschaft and Gentsch, 811
Rutten, 1605
Ruymbecke, 1159

SACCHI and Ranieri, 1051
Sachs, 1204, 1264, 1613
Sack, 372
Sadewasser & Co., 495
Sadler, 142
Sadler & Co., 83
Sadtler, 184
Salkowski, 267, 272
Salm, 1200, 1202
Salzer, 797, 798
Salzmann and Wichelhaus, 188
Sander, 1309, 1410
Sandgreen, 332
Sängerhäuser Aktien-Maschinenfabrik, 454
Santesson, 230
Santi, 1313
Sauer, 1471
Saunders, 1557
Savalle, 755, 914, 927, 932, 933, 934, 1381
Sawitsch, 219
Schacherl, 793
Schaefer, 42, 1015, 1449, 1514, 1609
Schaer, 273
Schaffer, 1061
Schauer, von, 28
Scheer & Co., 474
Scheibe, 60
Scheithauer, 186, 194, 896
Schelenz, 224
Schenk, 988
Schenk zu Schweinsberg, 578
Schenkel, 658, 660
Scherges, 809
Schering, 786
Scheurer-Kestner, 155
Scheurlen, 810
Schick and Aktien-Gesellschaft für Stickstoffdünger, 1131
Schiff, 1316
Schildhaus and Condera, 892
Schiller, 1152
Schilling, 325, 1046, 1185, 1189, 1190, 1201, 1202
Schilling and Kremer, 1160
Schlesische Kohlen-und Kokswerke, 96
Schlicht, 161
Schlickum, 797
Schliemann, 494
Schlosser, 386
Schlösser and Ernst, 718
Schlumberger and Piotrowski, 1304
Schlutius, 1231
Schmalz, 96
Schmatolla, 819
Schmetz and Schramm, 547
Schmidt, 226
Schmidt and Böcker, 1333
Schmidt and Chasseur, 137
Schmidt and Schulz, 289
Schmidtborn, 1531
Schmitt, 1018
Schmitz, 199, 1396
Schmitz-Dumont, 982
Schrauder and Bergmann, 546
Schneider, 215, 217, 718, 765, 811, 1159, 1378
Schneidt, 687, 692
Schniewindt, 30, 111, 132, 152
Schnitzler, 742
Schorrenberg, 1011
Scholl, 1606

Scholvien, 184, 226, 394, 602, 618
Schönbein, 1145
Schöndeling, 547
Schondorff, 9
Schönfeld, 1314
Schönherr, 1075
Schorlemmer, 210, 214, 218, 266
Schorr, 541
Schramm, 1043
Schreiber, 80, 85, 161, 865, 1020, 1088, 1164, 1237
Schroeder, 439
Schroeder and Berens, 812
Schryver, 793, 796
Schülke and Mayr, 811
Schuller, 623
Schulte, 1477
Schultz, 3, 16, 37, 232, 263, 509, 631, 635, 710, 921, 940, 948, 950
Schultz and Hartog, 211
Schultz and Papp, 640
Schultz, Perl, and Szekely, 238
Schultzen and Naunyn, 267
Schulz, 236, 688
Schulze, K. E., 177, 178, 226, 236, 237, 238, 247, 252, 265, 266, 275, 279, 286, 288, 295, 296, 306, 311, 313, 740, 856, 902, 920
Schumann, 1306, 1517
Schumann and Kuchler, 60
Schuster and the British Coke Ovens Co., 1196, 1332, 1483
Schutte, 552
Schützenberger and Ionine, 214
Schwab, 1473
Schwalbe, 937, 939, 985, 986
Schwarz, 277, 677, 882
Schwarz (Louis) & Co., 61, 410, 420
Schwarz and Bauschliger, 890
Schweissinger, 270
Schwerow, 231
Scott, 1449
Seeber, 1545
Seel, 811
Seidel, 1266, 1343
Seidenschnur, 654, 662, 687, 690, 69[illegible]
Seidler, 1566
Seiffert, 1463
Seigle, 193, 342
Seiler, 793
Sell, 732
Selwyn, 327
Semet and Solvay, 96, 99, 119, 131, 135, 136, 152
Semet-Solvay Co., 1482, 1605
Semmler, 313, 1601
Semper, 1049
Senger, 519, 520, 522
Serbowski, 1013
Serpek, 1076, 1097, 1102, 1103, 1104, 1105, 1107, 1108, 1109, 1610
Serret, 1057
Servier, 60
Sexauer, 875
Seyd, 661
Shakell, 693
Sharples, 160
Shaw, 323, 821
Shedlock, 360
Shipley, 441, 693, 704
Short, 115, 1243
Shukoff, 840
Sicard, 1043, 1154, 1526
Sicha, 766
Sidney, 558
Siebel, 119, 359, 848
Siemens, 719
Siemens and Halske, 1124, 1128, 1572, 1608
Siepermann, 1305
Siepmann, 7
Sifton and Harding Bros., 1607
Silbermann, 916
Simmersbach, 1186, 1192
Simon, 1608
Simon (Simon-Carvès), 91, 92, 96, 119, 126, 147, 148, 158, 197, 198
Simon and Watson Smith, 96, 1212
Sinclair, 1137
Sinding-Larsen and Storm, 1096, 1100
Sintier, 1458
Skirrow, 1285, 1286, 1493
Skraup, 298
Smet, 88
Smith, A., 813, 1167
Smith (Angus), 90, 119, 281
Smith, C. E., 793
Smith (H. F.), 60, 1587
Smith, J., 342
Smith (J. F.), 244
Smith, J. H., 1318
Smith (J. K.), 978
Smith (J. Weber), 363
Smith (Watson), 17, 41, 89, 90, 91, 97, 98, 145, 146, 148, 167, 176, 177, 179, 197, 213, 226, 265, 267, 278, 286, 292, 311, 317, 318, 323, 371, 379, 384, 400, 416, 449, 455, 500, 505, 513, 533, 554, 566, 570, 571, 603, 631, 648, 725, 734, 738, 740, 744, 745, 766, 788, 833, 844, 868, 884, 937, 970, 1188, 1208, 1309, 1319, 1343, 1367, 1438, 1469, 1486, 1513
Smith (W.), 1581
Smith and Albright, 56
Smith (Watson) and Chorley, 6
Smith (Watson) and Staub, 280
Smits and Postma, 1298
Snell, 1318
Società generale della Cianamide, 1140
Société l'Air Liquide, 1061
Société anonyme des combustibles industriels, 369, 712, 1597

Société l'Azote, 1091
Société d'Exploitation des appareils Rateau, 1588
Société Française de Fours à Coke, 1573
Société du Gaz de Paris, 1488
Société Générale des Nitrures, 1086, 1107, 1109, 1112, 1610
Société du Goudronnage des Routes, 365, 558
Société l'Hydrogène, 1062
Société Industrielle des Produits Chimiques Cuise-Lamotte, 1331
Société Lorraine de Carbonisation, 1480
Société Lorraine de Hussigny, 1255
Société anonyme des matières colorantes de St Denis, 938
Société anonyme des produits chimiques du Sud-Ouest, 1338, 1377
Société Oléo-graisse, 889
Société l'Oxydrique française, 1062
Sofianopulos, 1110
Soldenhoff, 96
Solomons, 1022
Solvay, 1047, 1066, 1345, 1362
Solvay Processes Co., 1536
Sommer, 390
Sonnenschein and Köhler, 546
Sorel, 79
Sospicio, 1023
South Metropolitan Gas Co. and Evans, 1123
Spakowski, 673
Spalteholz, 663, 817, 818
Spatjew, 16
Spence, 1499, 1547
Spence and Gilchrist, 1448
Spencer and Sisson, 1339
Speyer, 813
Spiegel, 1026, 1295, 1306
Spielmann and Wheeler, 1607
Spilker, 34, 51, 52, 114, 163, 266, 285, 427, 439, 454, 511, 542, 653, 747, 750, 767, 854, 863, 895, 936, 1005
Spilker and Bindewald, 972
Spilker and Dombrowsky, 241
Spilker and Weissgerber, 219
Spindler, 216
Sprenger, 658, 659
Spring, 1321
Staedel, 274
Staedel and Höltz, 278
Staedeler, 267
Staehelin, 230, 1029
Stähler, 1096
Stahlschmidt, 8
Starke, 194, 225
Stauber, 98
Stauber and Kochan, 1161, 1167, 1182
Stauf, 17, 87, 88
Staveley, 311, 314, 533, 572, 736, 818, 980
Stavorinus, 983
St Claire-Deville. *See* Deville
Steaua Romana Petroleum Co., 892
Steere, 61
Steffens, 1152
Stein, 851
Stein and Schwarz, 1272
Steinkohlenbergwerk "Lothringen," 656
Steinmetz, 1573
Steinmüller, 910
Steinhauser, 468
Steinherz, 1519
Stenhouse, 1022
Stenhouse and Grove, 831
Stephan, 813
Sternberg, 1151, 1152
Sterne, 1593
Steuart, 1491
Stevenson, 91, 1511
Stewart and Perry, 341
St Hilaire and Grousseau, 664
Stickstoffwerke Berlin, 1611
Stier, 96
Still, 80, 1237, 1345, 1483
Still and Lane, 316
Stine, 1379
Stinnes, 98
St Martin, 328
Stockholm's Superphosphate Fabrik Aktien-Gesellschaft, 1611
Stockmeier and Thurnauer, 789, 790
Stoermer, 283, 287
Stoermer and Boes, 250, 283
Stohmann-Kerl, 742
Stohmann, Kleber, and Langbein, 228, 254
Stöhr, 293
Stolle, 1051
Stolzenwald, 892
Stomps, 1128
Stone, 1605, 1607
Storck, 802
Storck and Strobel, 1548
Story, 814
Stringfellow, 368
Stroh and Osins, 1380
Ströhmer, 97
Ströhmer and Schultz, 91, 96
Strombeck, 1391, 1408
Strommenger, 825, 1238, 1530
Strutt, 1608
Stutzer, 1481
Stutzer and Stoll, 1142
Suburbaine, Soc. an., 1661, 1483
Sudheim and Koppen, 851
Sulphate of Ammonia Co., 1174, 1175
Sulzer-Rieter, 1123
Summerlee, 171, 176, 1251
Summers, 97, 1094
Sussmann, 675
Sutherland, 167
Sutton, 847

Süvern, 371, 812
Swindells, 1066, 1067, 1114
Swindells and Lancaster, 1246
Swiss Analytical Chemists' Society, 819
Swoboda, 818

TACK, 494
Taizo Kuroda, 393
Tammann, 247, 824
Tappeiner, 3
Tar Patent Solidifying and Distilling Co., 370
Tarbutt, 328
Tarless Fuel Syndicate, 47
Tatlock, 1248
Täuber and Löwenherz, 307
Tawildarow, 221, 222
Taylor, 185, 1696
Taylor and Walker, 1061
Tayne, 629, 694, 704
Technische Reichsanstalt, 1016
Teed, 1556
Teichmann, 1389, 1400
Teichmann and Bross, 676
Telle, 801
Tennessee Coal and Iron Co., 80
Teodorowitsch, 1191
Terres, 1028
Tervet, 1202
Tessié du Mosay, 1098
Testrup, Adam, Rigby, and Andrew, 1601, 1612
Thalwitzer, 718, 1029
Than, 1303
Theisen, 61, 1196
Thénard, 1301
Thenius, 295, 296, 297, 298, 559, 574, 665, 717, 856
Thenius and Weger, 294
Thiel, 1477
Thiele, 222, 242, 250, 626
Thiele, Parker, and Fincke, 883
Thilorier, 1389
Thiriart & Co., 483
Thomas, 9, 1596
Thompson, 327, 889, 1113
Thomsen, 1291, 1309, 1312, 1313, 1323
Thomson, 963
Thomson-Houston Co., 1095, 1096, 1610
Thomson and Tommasi, 1298
Thornton and Rothwell, 1018
Thorpe, 443
Thorsell, 1119
Tidy, 694, 698, 700, 702, 788, 1185, 1187, 1343
Tieftrunck, 63, 244
Tixier, 372
Toch, 391
Tocher, 803
Toldt, 419
Tommasi, 1309, 1611
Topf, 1552
Torfentgasung Stauber, 1182, 1612
Toth, 586, 789
Trachmann, 904
Train, 851
Traine and Hellmers, 1570
Trainer, 368
Tralls, 1147
Traube, 981
Traube and Biltz, 1322, 1572
Treadwell, 1283
Treddar, 546
Treumann, 1042
Trewby, 323, 955
Trewby and Fenner, 456
Trillich, 369
Trobridge, 291
Tröger, 1051
Trommsdorf, 809
Troost, 1301
Trouton and Andrews, 582
Truchot, 98
Tschelnitz, 281
Tscherniak and Günzburg, 1309, 1550
Tschudy, 1485, 1587
Tucker, 1095, 1110
Tucker and Moody, 1126
Tucker and Wang, 1126
Tufts, 1482
Twinch, 1068
Twynam, 1244
Twynam, Egham, and Matthews, 1160

UHL & Co., 1151
Uhlig, 405
Ulex, 1316
Ulsch, 1053, 1145
Ungnade and Nolte, 1135
United Gas Improvement Co., 180
United-Otto Coke-Oven, 115
United States Coke and Gas Co., 98, 111, 115
United States Geological Survey, 1591, 1593
United States Smokeless Powder Co., 1581
United States Steel Corporation, 32, 80, 1591
Universal Fuel Company of Chicago, 137
Unverdorben, 295
Urban, 1389, 1410
Ure, 382
Usher, 1304
Uyeno, 1064

VALENTA, 975
Valenta and Graefe, 645
Valpy and Lucas, 710
Vaubel, 307, 790, 802, 803
Vaughan, 448
Vautel, 643

Vedlé, 926
Veith, 673
Veith and Schestopal, 890
Verein chemischer Fabriken, Aussig, 1484
Verein für Beförderung des Gewerbfleisses, 1551
Verein zur Wahrung der Interessen der chemischen Industrie, 1078
Vereinigte Fabriken für Laboratoriumsbedarf, 519
Versfeld, 801
Versmann, 253
Veschy and Votocek, 618
Vibrans, 1149
Viganó and Soldi, 1612
Vincent, 200, 233, 389, 741, 742, 1149, 1150, 1155, 1160, 1458
Vincent and Delachanal, 265, 286, 305, 936
Vis, 1483
Voelcker, 700
Vogel, 67, 68, 1052, 1579
Vogler, 1318
Vogt, 873
Vohl, 243, 290, 481, 682, 690, 707, 828, 842
Voigt, 1124
Volger, 552
Volhard and Erdmann, 287, 288
Vongerichten, 294, 901
Vorster and Grüneberg, 1205, 1414
Vualflart, 1143
Vulpius, 797

WACHENDORF and Zincke, 255
Wächter, 1556
Wade, 1090
Wagener, 1476, 1478
Wagner, 608, 1046, 1066, 1124, 1140, 1199, 1274, 1517
Wahl-Gustrow, 1015
Wahlen and Caro, 1232
Wahlenberg, 1566
Wake and Ingle, 802
Walbinger, 360
Waldeck, 1204, 1213
Walker, 273, 1447
Walker and Smith, 507
Wallace and Wassmer, 1101, 1608
Wallbaum, 367
Waller, 273, 727, 800
Walter, 767
Wandel, 813
Wangenheim, 360
Wanklyn, 52, 443, 1201, 1257, 126[illegible]
Ward and Stanley, 1178
Wardell, 1598
Warner, 403, 406
Warnes, 425, 501, 508, 525
Warnes and Davey, 423
Warren, 210, 227, 233, 470
Warren Brothers, 367, 568
Warschauer, 1028
Warth, 1331, 1457
Wäser, 1610, 1611
Washburn, 1135, 1140, 1142, 1579
Wassermann, 686, 718
Waterman, 693
Watson, 1028
Weaver, 1131
Webb, 393
Wechselmann, 98
Wedekind, 1567
Wedemeyer, 1160
Wedge, 893
Wegelin, 716, 718
Weger, 227, 231, 233, 235, 236, 237, 238, 240, 243, 247, 248, 249, 257, 258, 274, 285, 295, 299, 300, 313, 627, 852, 920, 921, 936, 940, 943, 945, 965, 993
Weger and Billmann, 242, 261
Weidel and Ciamician, 268
Weigelt and Mehring, 750
Weil, 813
Weiler, 255
Weinmann, 1066
Weinreb, 798
Weintraub, 1096, 1610
Weise and Richa, 1064
Weiss, 154, 200, 931
Weiss and Engelhardt, 1097
Weissbein, 138
Weissgerber, 249, 266, 299
Weldon, 154, 155
Wellstein, 1255, 1475
Welsbach Co., 1496
Weltzien, 1305
Wenck, 1152
Wendriner, 368, 581, 583, 712, 905, 1333, 1488
Wendt, 247
Wermund & Co., 662
Wernecke, 494
Werner, 258, 1611
Werner and Pfleiderer, 494, 935
Westdeutsche Thomasphosphatwerke, 1093, 1148
Weston, 1056
Westphal, 328
Weyer, 241
Weyl, 267, 468, 481, 788, 817, 1029
White, 1132
White and Ball, 843
White and Hess, 51
White, Rowley, and Wirth, 62
Whitehouse, 1342, 1545
Whiteside, 1380
Wichelhaus, 247
Wien, 84[illegible]
Wilbrand and Beilstein, 233
Wildhagen, 355
Wiley, 1608, 1614
Wilhelm, 79, 865, 1488

INDEX OF NAMES

Wilhelm and Bohnstadt, 722
Wilke & Co., 494
Willgerodt, 938
Williams, 818, 1483
Williams, Greville, 65, 66, 204, 293, 296, 298, 300, 303, 304, 900
Williams, E. G., 557
Williams, Mackintosh, 942
Williams, C. E., 1123
Williams and Fenner, 1477
Williams and Ramsay, 1067
Willson, 1100, 1121
Wilson, 28, 233, 1247
Wilton, 392, 393, 460, 494, 507, 517, 1409, 1448, 1449, 1470, 1505, 1599
Winand, 1608
Winkelmann, 444
Winkler, 560, 1188, 1274, 1276
Winstanley and Williams, 1094
Wirkner, 368, 710
Wirth, 617, 621
Wischin, 216, 470, 746, 893
Wisse and Schneller, 193
Witt, 265, 396, 940, 1577
Wittenberg, 97
Wittstein, 1385
Witzek, 938, 1023
Wohl, 904
Wöhler, 267, 1051
Wolf, 495, 1111, 1194, 1213, 1238, 1253
Wolf, R., Aktien-Gesellschaft, 678
Wolff, 1029, 1176, 1177
Wolfram, 1199, 1457
Wolniewicz, 690, 891
Woltereck, 1068, 1069, 1173, 1174, 1175, 1178, 1180, 1231, 1253, 1303
Woltereck and the Sulphate of Ammonia Co., 1174
Woodbury, 1572
Woringer, 227
Wornast, 8
Wourtzel, 1304
Wrede, 341
Wreden, 214
Wright, 137, 316, 323, 347, 497, 533, 709, 1078, 1260, 1380, 1450
Wülfing, 1538
Wülfing, Dahl & Co., 1571
Wunder, 1377
Würth, 187
Württemberg Viticultural Institute, 808
Wurtz, 52, 200, 210, 268, 407, 622, 652, 653, 836, 862, 959, 1544
Wyant, 186
Wyatt, 322
Wylam, 540
Wyld, 419
Wyne-Roberts, 508

YOON, 766
Young, 55, 185, 193, 709, 881, 891, 1029, 1091, 1119, 1121, 1158, 1161, 1238, 1481
Young and Beilby, 1183, 1208, 1212, 1249
Young and Fortey, 229
Yvon, 271

ZALOZIECKI, 216, 297, 893
Zamore and Carlson, 1139, 1611
Zänker, 1110
Zeidler, 258, 630
Zeiss, 1608
Zelasko, 1611
Zelinski, 216, 289
Zellner, 718, 722, 723
Ziegler, 1172, 1173
Ziffer, 692
Zimmer and Gottstein, 187
Zimpell, 1475
Zincke and Breuer, 248
Zinrek, 812
Zmerzlikar, 252, 277, 398, 763
Znatowicz, 621
Zschokke, 80, 1240
Zwillinger, 97

INDEX OF SUBJECTS

ABSORBING-APPARATUS for ammonia vapours, 1381, 1382

Absorbing-oil, 607, 645

Accidents in tar-works, official recommendations of rules for preventing them, 103[illegible]

Acenaphthene, 248; recovery in tar distilling, 853

Acenaphthene hydride, 248

Acetic acid in coal-tar, 265

Acetone, 265; use for washing crude anthracene, 617

Acetophenone, 266

Acetylene, 218

Acetylene series, 218

Acids in creosote oil, Tidy's process for determining them, 699

Acid-tar for decomposing sodium phenolate, 744; running off, 878; acid-tar from washing tar-oils, 887; injurious properties, 887; utilization, 888; dilution with water, 888; preparation of asphalt from it, 889; various uses, 890; burning it for sulphur dioxide, 891; carbonization, 892; use for the manufacture of ammonium sulphate, 893; 1164, 1607

Examination of acid-tar, 894

Recovery of the pyridine bases from acid-tar. *See* Pyridine

Acridine, 300

Acridine, methylated, 301

Acridine hydrides, 301

Aërogen gas, 1026

Air-pressure for moving tar-oils, 431

Albo-carbon light, 845

Alcohols in coal-tar, 264; absolute alcohol made by fractionation with benzol, 10[illegible]9

Aliphatic hydrocarbons in crude benzol, estimation, 996

Allylene, 219

Aluminium nitride, as catalyzer for the synthesis of ammonia, 1102

Ammonia in coal-tar, 290

Ammonia, historical notes on it and its compounds, 1041, 1044, 1045; on its application, 1045; on its industrial production, 1045; increase of its application for agricultural purposes, 1046; manufacture from gas-liquor, 1017, 1257, 1260; from by-product coke-ovens, 1018; future of the ammonia industry, 1049

Ammonia, natural occurrence in soil, water, and air, 1050; in guano, 1050; in the suffioni, 1051; in volcanic products, 1051; in carnallite, 1051; in various rocks, 1052; formation by putrefaction, 1052, 1054; from nascent nitrogen and hydrogen, 1053; from nitrates, 1053; from atmospheric nitrogen, 1053; from cyanogen compounds, 1053; by the decay of organic substances, 1054; by destructive distillation, 1054

Synthetical production from nitrogen and hydrogen, 1048, 1064; by high temperatures, 1065; from steam and nitrogen, 1066; by catalysis, 1065; process of Haber, 1070; his patents, 1075; patents of the Badische Anilin- und Sodafabrik, 1076, 1079; processes for the synthesis of ammonia by various catalyzers, 1085; (iron, 1085; palladium, zinc, 1087; ruthenium, 1087, 1610; cerium nitride, 1087; titanium, 1088; vanadium, 1088); various catalyzers, 1088, 1609; apparatus, 1090

Synthesis of ammonia from nitrogen and hydrogen by the aid of the electric current, 1090

Production of ammonia from free nitrogen by the intervention of nitrides, 1095, 1610; (boron, 1095, 1610; silicon, 1096; titanium, 1097; magnesium, 1100; calcium, 1102; aluminium, 1102; Serpek's process, 1102; ferro-aluminium nitride, 1109, 1610; other aluminium processes, 1111; iron, 1112; various nitrides, 1112, 1610); by the intervention of cyanides, 1113; (historical, 1113; by cyanide of barium, 1114; Mond's process, 1115; by various cyanides, 1119; by calcium carbide and cyanamide [lime-nitrogen]), 1123 (*see* this); by titanium cyano-nitride, 1143; general, 1611; from nitrogen oxides and in various inorganic chemical processes, 1145

Recovered as a by-product in the manufacture of beetroot sugar (vinasse), 1148, 1612; from urine, sewage, etc., 1154; from guano, 1161; by carbonizing bones, horn, leather, wool, hair, and other animal substances, 1162; from peat, 1168, 1612; from bituminous shale, 1182; from coal, 1184, 1612; from spent oxide and other by-products of gas-works, 1206; from calcium-carbonate mud, 1207; from gasifying coal or shale by the action of steam, 1207, 1613; Mond gas-process, 1213; Lymn's gas-process, 1223; other gasifying processes, 1231, 1613

From coke-ovens, 1234, 1237, 1613; condensing-apparatus, 1240

Direct sulphate process, 1237

Recovery by means of sulphur dioxide, 1238

Recent improvements in the recovery of ammonia from coke-oven gases, 1243

Ammonia from blast-furnace gases, 1245; from producer-gas, 1252; from ordinary products of combustion (coal-smoke), 1254

"Fixed" ammonia, 1257, 1337

Estimation of ammonia in spent oxide, 1290

Physical properties, 1291, 1614

Ammonia, anhydrous liquid, properties, 1292; degrees of cold produced by it, 1294; solvent powers, 1294; behaviour to water, 1295; hydrates of, 1298; solubility in other liquids, 1299; absorption by solid substances, 1300; chemical behaviour, 1301; decomposition by the electric current, 1301; by heat, 1301; by light, 1304; by radium emanation, 1304; combustibility, 1305; behaviour towards various elements and oxides, 1305; towards other gases and liquids, 1306; physiological properties, 1307; use for washing crude anthracene, 617

Manufacture, 1388; historical, 1388; general principles, 1389; purification of the gaseous ammonia before compression, 1390; testing it for moisture, 1391; intermediate vessels, 1393; compressors for liquefying, 1394; cooling of the compressed gas, 1395; collector, 1396; combination of apparatus, 1396; apparatus of the Germania Engineering Works, 1396; of the Maschinenfabrik Sürth, 1397; of Teichmann, 1400; various processes, 1403

Storage and carriage of liquid ammonia, 1404; rules of the German Railway Companies, 1405; of the English Board of Trade, 1406; filling of the drums, 1406; discharging-valves, 1407

Properties of commercial liquid ammonia, 1408; applications, 1409; analysis, 1410

Ammonia, aqueous solutions of, specific gravities, 1297; vapour-pressures, 1298; chemical behaviour, 1307

Ammonia, solid, 1383

Ammonia vapours, absorption in water, 1380; by hygroscopic salts, 1383

Ammoniacal liquor, composition, 1256; influence exerted on it by the style of the gas-retorts, 1258; by the washing out of the hydrogen cyanide, 1258; by the oxidizing action of the air, 1259; analyses by Linder, 1260; distribution of sulphur, 1263; of cyanogen, 1263; recovered sulphur, 1264; analyses by Mayer and Hempel, 1265

Valuation of the hydrometer, 1266; by chemical methods, 1266; estimation of volatile ammonia, 1267; of total ammonia, 1269; methods for the use of workmen, 1269; accurate methods (distillation test), 1270; choice of the acid for titration, 1278; of the indicator, 1274; azotometric test, 1274; complete analysis, 1277, 1289

Working it up, 1326; separating from the tar, 1326; storage, 1329, 1614; working it up without distillation, 1329; direct use as manure, 1329; direct saturation with acids, 1329

Treatment with calcium or magnesium sulphate, 1330; with kieserite, 1332; with coal-gas, 1332; conversion into nitric acid, 1332

Removal of the cyanides before distillation, 1333

Removal of the tar-fog before treating the gases for ammonia, 1335

Distillation, 1336; question of boiling with or without lime, 1336; use of other compounds for liberating the ammonia, 1341

Distillation. *See* Stills

Various products made from it, 1343; concentrated gas-liquor, 1344; various apparatus, 1344; apparatus of Solvay, 1345; of Grüneberg, 1347; of Grüneberg and Blum, 1351; of the "Bamag," 1351; other apparatus, 1358; special processes, 1358, 1614; concluding remarks, 1359

Manufacture of pure liquor ammoniae, 1360; removal of hydrogen sulphide and carbon dioxide without lime, 1361;

method of Pfeiffer, 1362; of Solvay, 1362; of Julius Pintsch, 1365; purification from empyreumatic (tarry) substances, 1366; apparatus for the manufacture of liquor ammoniæ, 1368; simple apparatus, 1368; of Elvers and Pack, 1370; of the "Bamag," 1373; of Hirzel, 1374, 1375; of Feldmann, 1375; of Mallet, 1375; various, 1377
  Carriage and storage of ammoniacal liquor, 1383, 1614; in glass carboys, 1383; in iron drums or tank-wagons, 1384; localities for storage, 1384
  Uses of liquor ammoniæ, 1384
  Testing of liquor ammoniæ, 1385
  Reception, transportation, and storage, 1489
"Ammoniakprober," 1269
Ammonias, substituted, 291
Ammonium acetates, 1325, 1581
Ammonium bromide, 1545
Ammonium carbamate, 1316
Ammonium carbonates, historical notes, 1041, 1043; various properties, 1315; commercial carbonate of ammonia, properties, 1317; solutions, 1318; various carbonates, 1552; formation, 1552; manufacture, 1552; resublimation, 1554; drying, 1555; various methods of manufacture, 1556; use of calcium-carbonate mud, 1559; pure commercial ammonium carbonate, 1560; applications, 1560; statistics, 1560
Ammonium chlorate, 1321
Ammonium chloride (*see* Sal-ammoniac), properties, 1312; specific gravity of solutions, 1312; action on metals, 1313; reactions, 1313
  Manufacture, 1526; by direct saturation of gas-liquor with hydrochloric acid, 1527; from the sulphate, 1530; other processes, 1532; from waste liquors of ammonia-soda works, 1534; various processes, 1536, 1615
  Properties of crude ammonium chloride, 1538
  Sublimation, 1539; pure crystallized muriate of ammonia, 1543; purification from iron, 1544
  Uses, 1544; statistics, 1545
Ammonium chromates, 1324, 1580
Ammonium cyanide, 1311
Ammonium ferrocyanide, 1311, 1547
Ammonium fluoride, 1314, 1545
Ammonium formate, 1325, 1581
Ammonium nitrate, properties, 1322; manufacture, 1561; from liquor ammoniæ and nitric acid, 1562; by decomposition of other ammonium salts with nitrates, 1563; by oxidation of ammonia, 1572; various methods, 1572; statistics, 1573; preparation in the granular state, 1573; examination, 1573
Ammonium nitrite, 1322, 1561
Ammonium oxalates, 1325
Ammonium perborate, 1577
Ammonium perchlorate, 1325, 1576, 1582
Ammonium persulphate, 1321, 1574
Ammonium phosphates, 1324, 1578
Ammonium sulphate manufacture, 1414; older process, 1414; Coffee still, 1416; horizontal cylindrical stills, 1423; continuous saturation apparatus, 1424; Dutch apparatus, 1426; apparatus of A. Mallet, 1427; of Grüneberg, 1432; of Grüneberg and Blum, 1435; of Hirzel, 1443; of Feldmann, 1439; of Pintsch, 1443; of P. Mallet, 1446; various forms of ammonia stills, 1447; obtaining ammonium sulphate free from cyanides, 1450; treatment of ammoniacal liquor in the cold state for removing hydrogen sulphide and carbon dioxide, 1454; apparatus for working sewage (*see* this)
  Absorption of the vapours in sulphuric acid. *See* Saturators.
  Various processes for producing it, 1483, 1614
  Coloration, 1485
  Draining on benches or by centrifugals, 1487
  Store-rooms for it, 1488; granulating, drying, and screening, 1488; packages, 1489
  Concentration of solutions, 1511; smell arising in this operation, 1512
  Manufacture otherwise than from ammoniacal liquor, 1512
  Examination of commercial sulphate of ammonia, 1513; percentage of nitrogen or ammonia, 1513; table for comparing these, 1514; moisture, 1514; free acid, 1514; colour, 1514; impurities, 1516; sulphocyanide (thiocyanate), 1516; organic compounds injurious to plant life, 1517; prescriptions laid down in sale-notes, 1517
  Applications, 1518
  Statistics for Great Britain, 1520; 1614; United States, 1522, 1615; Germany, 1523; other countries, 1524, 1615; world's production, 1525
Ammonium sulphates, various, properties, 1319; specific gravity of solutions, 1320
Ammonium sulphides, 1310
Ammonium sulphites, 1321, 1480
Ammonium sulphocyanide (thiocyanate), properties, 1310; preparation, 1547; applications, 1551; analysis, 1552
Ammonium thiosulphate, 1321, 1378
Amylene, 213

Animal substances, recovery of ammonia in carbonizing them, 1162

Aniline in coal-tar, 291

Anthracene, 250; discovery, 250; constitution, 251; formation, 251; preparation in the pure state, 252, 621; properties, 253; prepared by distilling pitch, 570; new uses of, 624; yields, 627; statistics, 628; prices, 629

Anthracene hydrides, 254

Anthracene, crude, quality, 590; percentage of pure anthracene in it, 591; crystallization of crude anthracene, 593; cooling the anthracene oil, 593; filtering the cooled oil through bagging, 594; through filter-presses, 596; by aspirating-machines, 597; by centrifugal machines, 598; by hydraulic presses, 598; application of heat, 599; various methods of filtering, 602

Treatment of the oils filtered from crude anthracene, 602; carbolineum, 605; employment of anthracene oil for removing naphthalene from illuminating-gas, 607; for the construction of basic linings in steel-works, 608

Washing the pressed crude anthracene, 609; with solvent naphtha, 609; with petroleum spirit, 612; with creosote oil, 612; with paraffin oil or oleic acid, 615; with pyridine bases, 615; with various agents, 616; danger of fire, 618

Anthracene, crude, purification by fusion with caustic potash, 618; dehydration, 621

Disease afflicting the men employed in the purification of anthracene, 622

Subliming the anthracene, 622

Synthesis of anthracene, 624

Properties, 630; composition of crude anthracene, 630; analysis, 632; sampling, 633; anthraquinone test, 633; Höchst test, 634; other methods, 634; estimation of the quantity of anthracene present in tar, 639

Detection and estimation of the impurities contained in commercial anthracene, 640; imido-phenylnaphthyl, 640; methylanthracene, 640

Anthracene oil, 450, 451; composition, 589; method of working it up, 589

Anthraquinone test for the estimation of anthracene, 633; Höchst test, 634

Anthrisol, 372

Anthrol, 279

Antinonnin, 811

Antiseptic application of coal-tar, 371

Argon, 606, 1124

Armoniacum, 1042

Aromatic addition products, 214

Arsenic, removal in the manufacture of ammonium sulphate by the use of acid-tar, 893

Ashes, estimation in coal-tar, 526

Asphalt, manufacture from tar without distillation, 368; in tar-distilling, 451; percentage of it in coal-tar, 532; nature of pitch-asphalt, 535; statistics, 555; distinguishing natural from tar-asphalt, 585, 1601; employments, 556; for street-paving, 556, 562, 1601; for insulating cables, 563; testing bituminous binders for asphalt paving, 581; asphalt from acid-tar, 889

Asphalt paper, 562

Asphalt pipes, 561

Asphalt, natural, distinction from coal-tar asphalt, 585

Astatki, 190, 329

Aurin. *See* Rosolic acid

Autin, 1028

Avenarine, 605

Azotometer, 1274

BACTERIA for converting nitrogen into ammonia, 10[illegible]

Bacterial treatment of waste ammonia liquors, 1493

Bakelite, 814

Barium carbide for the synthetic production of aromatic hydrocarbons, 195

Barium cyanide, use for the manufacture of ammonia, 1114

Barol, 606

Bases contained in coal-tar, 290; in light oil, testing for, 957

Beetroot sugar, formation and recovery of ammonia in its manufacture, 1148

Bellite, 1030

Benoid gas, 1026

Benz-asphalt, 352

Benzene, 223; discovery, 223; in coal-tar, 225; formation, 226; properties, 227; theoretical importance, 228; solubility, 229; illuminating power, 229; toxic properties, 230; chemical behaviour, 231

Preparation in the pure state by special stills, 922, 936; by solidification, 940

Benzene series, 222

Benzerythrene, 263

Benzoic acid as a by-product in the manufacture of carbolic acid, 741; manufacture from light oil, 856

Benzol, recovery of this contained as vapour in coal-gas, 64, 1589; from coke-oven gases, 70; in the shape of nitro-benzol, 82; composition of benzol recovered from coal-gas, 83; estimation of benzene and its congeners in coal-gas, 85, 1590; development of the extraction of benzol from coke-oven gases, 155, 1593; from petroleum, 1594, 1595; distinction from benzene, 224 (*see* this), 1596

Benzol, crude, from light oil, 863; from coke-oven gases, 865; properties of this, 1596

Deodorizing benzol, 919; rendering it non-explosive and non-inflammable, 919

Composition and properties of commercial benzols, 948, 954

Pure benzol, requirements for, 955

Benzol, commercial, testing methods, 958, 1607; by fractional distillation, 958 (*see* this), influence of carbon disulphide, 970; determination of toluene, 971; specific gravities, 972; testing for paraffin (*see* this), for petroleum, or shale-spirit, 973; nitrating test, 975; titration with bromine, 977; testing with concentrated sulphuric acid, 978; for the smell, 980; examination for carbon disulphide, 980 (qualitative, 980; quantitative, 981; by conversion into xanthogenate, 982; other methods, 983); for thiophens, 984 (qualitative, 984; quantitative, 985); for total sulphur, 987; for pyridine and other bases, 988

Estimation of the real composition of commercial benzols, 989; fractional distillation, 988; testing for toluene in "pure benzene," 992

Preventing the formation of explosive mixtures with air, 1008

Storage, 1007; carriage, 1010; moving about in the factories, 1011; apparatus for filling casks safely, 1011

Applications, 1012; various, 1012; as solvent, 1012; for india-rubber, 1012; as detergent, 1013; for varnishes, 1014; for the removal of naphthalene from coal-gas, 1015; for denaturing spirits, 1015; as illuminant, 1017; mixing with petroleum spirits, 1019; use in miners' lamps, 1019; for carburetting gas, 1021; for driving motors and motor-cars, 1027, 1607; for various other purposes, 1028

Statistics, 1030, 1607; fluctuations in prices, 1032

Benzol-magnesia, 1013

Benzonitrile, 306

Bithulic pavement, 558

Bitumens, 264

Bituminous substances in pitch, testing for, 582

Black-ash, formation of cyanides and ammonia in its manufacture, 1147

Blast-furnace gases, tar and ammonia from, 169; Gartsherrie process, [illegible]; composition of blast-furnace tar, 176; uses, 178; apparatus for the recovery of ammonia from them, 1245

Blue-steaming of bricks, 311

Boron nitride for the production of ammonia, 1095

Break in the distillation of tar, 445, 446

Brickwork, painting with tar, 349

Brimstone, application in the last stage of tar distillation, 457

Brimstone-acid for manufacturing sulphate of ammonia, 1465

Briquettes made with tar, 360; with pitch (*see* Patent fuel)

Bromine test for benzol, 997, 1005

Brunolic acid, 281

Burning-naphtha, 921; properties, 921

Butadiene, 219

Butane, 209

Butylene, 213

By-product recovery coke-ovens. *See* Coke-making

CALCIUM carbide and cyanamide (lime-nitrogen, Kalkstickstoff), 1123, 1611; historical notes, 1123; scientific laboratory investigations on the fixation of nitrogen by the carbides of alkaline-earth metals, 1125; manufacture of pure calcium carbide, 1127; technical processes for the preparation of calcium carbide and cyanamide (lime-nitrogen), 1127; processes of Frank and Caro, 1128; other processes, 1131, 1610, 1611; uses of lime-nitrogen, 1137; production of ammonia from calcium cyanamide, 1137, 1611; of cyanides, 1140; of graphite, 1140; storage of calcium cyanamide, 1140; statistical notes, 1140; analytical methods for cyanamides, 1142

Calcium-carbonate mud, ammonia from, 1207

Calcium nitride as catalyzer for the synthesis of ammonia, 1102

Carbazol, 307, 612, 615, 627; estimation, 642; discovery, 644

Carbenes, 531

Carbolic acid, properties. *See* Phenol

Manufacture, 731; treatment of the carbolic oil or middle oil with caustic potash or soda, 731; with lime, 732; quantity and strength of alkali employed, 732; fractional saturation, 733; prescription of Lowe, 733; other prescriptions, 734; treatment of middle oil with a mixture of lime and sodium sulphate, 735; with hydrated lime, 737; mixing of the carbolic oil and the alkaline liquid, 737; mixing-vessels, 738; oil drawn off from the sodium phenolate, 740; further treatment of the carbolic oil, 741; recovery of benzoic acid from it, 741;

treatment of the liquor containing sodium phenolate, 741; removal of impurities, 741; decomposition by mineral acids, 741; use of sulphuric acid, 744; of acid-tar, 744; of hydrochloric acid, 745; of sulphurous acid, 745; of carbonic acid, 746; of sulphuretted hydrogen, 749; dealing with the solution of sodium sulphate, 749

Working up the crude carbolic acid, 749; washing it, 750; waste-water, 750

Manufacture of pure carbolic acid, 750; first distillation, 750; various apparatus, 751; distillation of mother-liquors, 755; crystallization of the distillate, 755; manufacture in England, 758; prevention of nuisance, 760; covered receivers, 760; absolutely pure carbolic acid, 762; synthetic production of carbolic acid, 764, 1605

The reddening of carbolic acid, 765; causes of it, 766; processes for preventing it, 770

Liquid carbolic acid, 773

Yield of pure products from crude carbolic acid, 779

Methods for examining carbolic oil (middle oil) and carbolic acid of various grades, 781; estimation of the total phenols, 782; of the crystallized phenol, 782; solidifying-point, 782; amount of bases, 784; of pyridine bases, 784

Commercial forms of carbolic acid and the cresols, 785; crude carbolic acid, 785; crystallized phenol, 785; liquid crude carbolic acid, 785; pure cresols, 785; crude commercial carbolic acid, 786

Testing of crude carbolic acid, 786; approximate estimation of phenol, 786; method of Lowe, 787; other methods, 788; estimation of water, 790; of naphthalene, 792; various methods, 793; discovery of paraffin, 794

Examination of pure phenol and cresols, 705; fusing-points, 795, 796; contents of water, 795; solubility, 797; sulphur compounds, 797; distinction of liquefied pure carbolic acid, 797

Exact quantitative estimation of phenol as tribromophenol, 798; method of Koppeschaar, 799; similar methods, 800; other methods, 803; methods for estimating the three cresols, 803

Determination of phenols in gas-liquor, 1285

Commercial preparations made from carbolic acid and cresol, 806; carbolic-acid soaps, 807; soluble carbolic-acid preparations of non-soapy character, 809; carbolic-acid powders, 811; carbolic-acid tablets, 812

Poisonous action of carbolic acid and cresols, 813

Condensation-products of phenols with formaldehyde (bakelite, resinite), 813

Analysis of carbolic-acid preparations, 815

Applications of carbolic acid and of the cresols, 821; for medical and antiseptic (disinfecting) purposes, 821; for technical purposes, 822

Statistics, 823, 1605

Carbolic oil, 448, 651, 724, 1602; composition, 724; properties, 725; working it up, 725; redistillation, 726; fractions made in this, 728; cooling it down and obtaining naphthalene, 729; treatment of the oils draining from this, 731; treatment for carbolic acid (*see* this)

Carbolineum, 593, 605; examination, 645

Carbol-lysoform, 662

Carbon, free, in coal-tar, 308, 452; estimation of it, 508, 523; purification of the tar from it, 394; cause of boiling-over in the distillation, 438; in pitch, 531; estimation in pitch, 575; manufacture from pitch, 1602

Carbon dioxide, removal from liquor ammoniæ, 1358, 1361

Carbon disulphide in coal-tar, 286; in benzol, 936; removal, 937; influence in testing benzol by distillation, 970; examination for, 980 (*see* Benzol)

Carbon oxysulphide, 287

Carbonic acid for decomposing sodium phenylate, 746

Carbons, electric, made from pitch-coke, 572

Carbosprit, 1020

Carbures in pitch, 531

Carburetting-gas by tar-oils, 1021

Carburetting-naphtha, 918

Carburetting water-gas by benzol, 1024; valuation of tar-oils for this purpose, 1026

Carnallite, ammonia from, 1051

Carriage of coal-tar in boats, 376; in railway trucks, 376; in wooden or iron casks, 378; of benzol, 1010

Catalyzers for the union of hydrogen and nitrogen, 1065, 1074, 1077

Centrifugal machines for filtering crude anthracene, 598; for draining the mother-liquor from ammonium sulphate, 1487

Cerium oxide for obtaining free ammonia, 1042

Cerium nitride as catalyzer for the synthesis of ammonia, 1087

Cespitine, 291

Chrysene, 260

Chrysene hydrides, 261

Chrysogen, 261

Claus process for treating the gases from ammonia saturators, 1500, 1511
Coal, formation, 1; properties, 4; composition of various classes of coal, 5; resinous and wax-like substances contained in coal, 7; dissolving action of pyridine, 8; of bromine, 9; gases contained in coal, 9
  Occurrence of coal in nature, 9; production of the principal countries, 10; entire stock of coal in the earth, 10; proportion of coal used with recovery of tar, 11
  Destructive distillation of coal, 11; solid residue, 12; permanent gases formed, 12; watery distillates, 12; tar, 13 (*see* this), 1587
  Ammonia from coal, 1184; percentage of nitrogen in coal, 1184; production of ammonia in the manufacture of coal-gas and coke, 1185; yield of ammonia in the manufacture of coal-gas, 1187; influence of temperature, 1191; special processes for the treatment of coal-gas for ammonia, 119[illegible]; processes for increasing the yield of ammonia in gas-making, 1200; "liming," 1200; by means of hydrogen, 1202; by means of steam, 1203; ammonia from coal gas directly, without scrubbers, 1204; gasifying coal by the action of steam (producer-gas, Mond gas), 1207
Coal-gas, ammonia from, 1187
Coal-smoke, ammonia from, 1254
Coal-tar. *See* Tar, Gas-tar
Coke breeze, working it up by the Lymn gas process, 1227
Coke-making, with recovery of tar and ammonia as by-products, 87; statistics, 94, 1590, 1591; enumeration of patents, 95; description of the most important forms of by-product recovery coke-ovens, 98, 1592; modified beehive ovens, 99; Jameson ovens, 99; Otto ovens, 103; modified Coppée ovens, 104; ovens of Lürmann, 104; of Otto-Hoffmann, 105; of Otto-Hilgenstock, 111; other ovens of that class, 117; modified Carvès ovens, 119; Simon-Carvès ovens, 119; Hüssener ovens, 127; Semet-Solvay ovens, 131; other ovens, 136, 1593; coke made from coal-tar, 373
Coke-oven gases, benzol from, 78, 155 (*see* Benzol); ethylene from, 157; illuminating-gas from, 158; washing-oil from, 865
Coke-oven tar, quality, 145; from Jameson ovens, 146; from Simon-Carvès ovens, 147; from Otto-Hilgenstock ovens, 148; from United-Otto ovens, 151; from various ovens, 152; general conclusions, 154; statistics, 161; results of working it up, 946
Coke-ovens, ammonia from, 1234, 1237; condensing-apparatus for it, 1240; improvements in the process, 1243
Coking in the distillation of tar, 453
Coking-residue of coal-tar, estimation, 526; of pitch, 576
Collidines, 297
Colour of sulphate of ammonia, 1485, 1514
Columns for rectifying benzol, etc. *See* Stills
Columns for laboratory use, 996
Combustion gases, ammonia from, 1254
Combustion of gases from ammonia saturators, 1497
Compressors for liquefying ammonia, 1394
Condensed water from ammonia saturators, 1490
Condensing-plant for tar and ammonia connected with coke-ovens, 138; for tar-stills, 421; cooling-worms, 422; choice of metal for these, 422; cement for the joints, 425; various constructions of cooling-apparatus, 426; receivers, 428; separating-box, 428; store-tanks, 430, montejus, 431; explosions, 431; treatment of the escaping gases, 432
  For the ammonia from coke-ovens, 1240
Contact action for uniting nitrogen and hydrogen. *See* Catalyzers
Contact poisons, 1077, 1082
Continuous distillation of tar, 481
Continuous saturation for sulphate of ammonia, 1424
Coolers for benzol stills, 935; for ammoniacal vapours, 1382
Cooling-worms for tar-stills, 421
Coridines, 297
Coumarone-resin, 905
Crackene, 264
Cracking heavy tar-oils, 706
Creoline, 658, 773; analysis, 817
Creosote-oil, 451; use for washing crude anthracene, 612; treatment for the extraction of phenols and naphthalene, 647; properties, 648; composition, 648; results of distillation, 648; storing it up, 649; store-tanks, 650; separation of naphthalene, 650; carriage, 651
  Redistillation, 651, 653; naphthalene oils, 652
  Cooling and separation of naphthalene, 653
  Fractions obtained in redistillation, 653
  Special processes for treating it, 654; removing the pyridine bases, 654; removing the smell, 655
  Antiseptic properties, 656; disinfecting powders, 657; mixtures with chloride of zinc, 657
  Emulsions, 653; creoline, 658; lysol,

660; similar preparations, 661; lysocresol, 661; lysoform, 661; lysosulphol, 662; carbol-lysoform, 662; sapophenol, 662; Boleg's emulsion with rosin oil, 662; westrumite, 662; other emulsions, of creosote oil, 663, 664; emulsions produced by sulphuric acid, 663

Employment as a lubricant (cart-grease, etc.), 664; removal of the phenols, 665

Employment for lighting, 666; construction of lamps, 666; lamp of Hartmann and Lucke, 666; of Lyle and Hannay (lucigen light), 668; Grube's oleo-vapour lamp, 671; Luther and Rose's portable sunlight, 672

Application of creosote oil as fuel, 672; advantages of it, 672; evaporating-power, 673; for raising steam, 674; conversion into a spray, 675; for smelting metals, 676; for fusing metals in crucibles, 676; for chlorinating-roasting, 677; for other metallurgical purposes, 677; as fuel in explosion motors and in caloric engines, 678

Application for pickling timber, 679; historical notes, 679; apparatus employed, 681; difficulty caused by the moisture in the timber, 682; apparatus of Boulton, 683; various apparatus, 684; process of Rutgers, 685; modern evacuating-processes, 686; Rüping process, 686; various apparatus, 688; special treatment of creosote oils for pickling timber, 688, 1602; advantages of creosoting timber, 689; experiences made with telegraph poles, 692; with railroad sleepers, 692; part played by the naphthalene in pickling timber, 694

Prescriptions concerning the quality of tar-oils, to be used for pickling timber, 695; by Allen, 696; by various works, 696; report of Boulton, 697; of Tidy, 698; of Abel, 701; tests prescribed by him, 701; tests made at the works, 703; specification for Prussian railroads, 703; in the United States, 704; testing methods, 705

Decomposition of heavy tar-oils by heat (cracking), 706

Application for the "blue-steaming" of bricks, 711

Various other applications, 712

Manufacture of lampblack or soot, 712 (*see* Lampblack)

Statistics on creosote-oil, 723

Creosoting timber, 679 (*see* Creosote oil)

Cresochin, 809

Cresolimentum, 808

Cresoline, 658

Cresols, 274; isomeric crysols, 274; properties, 275; comparison of properties with those of carbolic acid, 275; commercial cresols, 772; composition, 772; properties, 773; poisonous and antiseptic properties, 774; separation of the three isomeric cresols, 775; cresol obtained synthetically, 780; commercial pure cresol, 785; technical metacresol, 786

Reactions for distinguishing phenol and cresols, 786

Analytical methods. *See* Carbolic acid applications, analytical methods

Commercial preparations made from cresol. *See* Carbolic acid

Crotonylene, 219

Crude-benzol still, 886

Cumanollack, 554

Cumarone, 282

Cumene, 236, 238

Cyanamide. *See* Calcium carbide

Cyanides, use for the preparation of ammonia from nitrogen, 1113, 1119; manufacture from lime-nitrogen, 1140; by means of titanium cyanonitride, 1143; formed in the black-ash manufacture, 1147; determination, 1284

Removal from ammoniacal liquor, 1383; from ammonium sulphate, 1450

Cyanogen compounds in coal-tar, 305; ammonia from, 1053

Cyclopentadiene, 221

Cylline, 808

Cymene, 238

DAHMENIT, 851

Decane, 210

Dehydration of tar before distilling it, 384; by settling, 384; by centrifugalling, 386; by heat, 388; by chemical methods, 393, 438

Denaturing alcohol by coal-tar, 373; by benzols, 1015

Disinfecting mixtures from coal-tar, 371; from benzol, 1029

Diaphtherin, 809

Diesel motors fed with tar, 349

Dimethylpyridines, 296

Dinsmore process, 317

Dioxydiphenyl, 285

Diphenyl, 249

Diphenylene oxide, 284

Diphenylene sulphide, 289

Dippel's oil, 1162, 1164, 1165

Direct sulphate process, 1236

Disease afflicting the men employed in the purification of anthracene, 622

Distillation of coal-tar, 374; historical notes, 374; by steam, 381; naphtha obtained, 382; distillation by fire, 383; dehydration, 384, 1598 (*see* Tar-stills, working them)

Distillation of tar for the purpose of making illuminating-gas, 495; other methods of distilling tar, 498, 1599; removal from hot distillation gases, 1591; purification by treating with oxygen, 1598; removal of ammonium salts before distillation, 396

Distillation, fractional, for testing commercial benzol, 958; French standard apparatus, 958; English method, 960; uncertainties, 961; Lunge's investigation, 961; Bannow's report of the German committee, 964; various prescriptions, 965; German standard method, 966

Doerrite, 364, 558

Duodecane, 211

EMPYREUMATIC substances, removal from ammonia gas, 1366

Ethane, 209

Ethylbenzene, 237; estimation, 993

Ethylene, 212

Ethylene from coke-oven gases, 157

Ethylene series, 211

Ethyltoluenes, 238

Explosions in tar-reservoirs, 380; in condensing-apparatus of the stills, 431; in tar-stills, 447; in running off the pitch, 475

Explosive mixtures of benzol and air, preventing their formation, 1008, 1009; safety-explosives manufactured from nitro-derivatives of benzol hydrocarbons, 1030

FERRIC nitride as catalyzer for the synthesis of ammonia, 1112

Ferrocyanide, determination, 1280

Filter-presses for anthracene, 596

Filtering cooled anthracene oil, 594

Fires in pitch-houses, 475; apparatus for preventing them, 475; in localities for the treatment of crude benzol and naphtha, 884; means for extinguishing them, 884

First runnings in tar-distilling, 441; description, 866; testing by fractional distillation, 866; chemical treatment with sulphuric acid, 869; with alkali, 871; mixing-apparatus, 871; operation of mixing, 876; with sulphuric acid, 876; running off the waste acid, 878; washing with water, 878; second alkaline treatment, 879; colour of crude benzol, 880; testing by distillation, 880; other processes for treating the light oil, 880; with Nordhausen oil of vitriol, 882; with nitric acid, 882; with sulphur, 883; locality for the chemical treatment of crude benzol, 884; extinction of fires, 884; treatment of the washed naphtha, 885; distillation, 886

Working up into final products, 906; distillation by steam, 906; English steam-stills, 907 (*see* Stills)

Fishing-box, 1468

Fluoranthene, 258

Fluorene, 249, 625

Fördite, 1030

Formaldehyde, condensation-products with phenol, 813

Forsunka, 329

Fractional distillation, nature of, 443 (*see* Distillation)

Fractions in tar-distilling, 440; first fraction, 445; light oil, 445; carbolic oil, 448; middle oil, 449; creosote oil, 450; anthracene oil, 451; end of the distillation, 451; pitch, 453 (*see* this)

Fractions from benzol stills, 916; French style, 919

Fractionating-apparatus for laboratory testing, 994, 996

Fuel, use of coal-tar as, 322

GARTSHERRIE process, 171

Gas-liquor, use for the manufacture of ammonia, 1047 (*see* Ammoniacal liquor)

Gas-producers, tar and ammonia from, 167; Mond's, 1217; Lymn's, 1225

Gas-tar, production, 37; influence of the temperature on its quality, 38; differences among the tars from various raw materials, 41; working-temperatures at various gas-works and their influence on the quality of the tar, 42; influence of the shape of the retorts, 46; of the pressure within the retort, 47; of the quality of the coal, 48; of boghead, bituminous shales, cannel coals, 49; results obtained by Bunte and other observers, 50

Yield of tar from the coal, 52; proposals for increasing the quantity or improving the quality of tar in the manufacture of coal-gas, 54; recovery of the tar suspended in the gas, 56; process of Pelouze and Audouin, 58; other apparatus for this purpose, 59

Gases contained in coal, 9; evolved in distilling tar, 432, 439; escaping from the saturators, 1496

Gasifying processes, various, 1231

Gasin, 852

Gas-volumes, reduction to normal conditions, 1276

Gas-volumeter, 1276

Graphite recovered in the manufacture of lime-nitrogen, 1140

Guano, ammonium carbonate from, 1050; ammonia from, 1161

Gum ammoniac, 1042

HEAP-COAL, working up by the Mond-gas process, 1221
Heating by burning coal-tar, 322
Hemellithol, 237
Heptane, 210
Heptylene, 214
Hexane, 209
Hexoylene, 221
Hexylene, 214
Höchst test for anthracene, 634
Huile sidérale, 653
Hydraulic presses for crude anthracene, 598
Hydrindene, 242
Hydrocarbons from Pintsch gas, 66; from coal, 1587
Hydrochloric acid for decomposing sodium phenylate, 745
Hydrogen, preparation, 1059, 1608, 1609; transportation, 1609; mixtures of hydrogen and nitrogen, 1064
Hydrogen sulphide, removal from liquor ammoniæ, 1358, 1361; from the saturator gases, 1503
Hydrometer, use for the valuation of ammoniacal liquor, 1266

IDRYL, 258
Illuminating-gas from coke-ovens, 158; from coal-tar, 316; Dinsmore process, 317; other processes, 319; opinions on the practical value of making illuminating-gas from coal-tar, 495
Imido-phenylnaphthyl, 640
Indene, 240
Indicators for titrating ammonia, 1273, 1274
Indol, 301
Inert gases, distilling the tar in a current of them, 468
Iridium as catalyzer for the synthesis of ammonia, 1090
Iron for tar-stills, 397, 564; as catalyzer for the synthesis of ammonia, 1085; iron vessels for ammoniacal liquor, 1384; protection, 1384

Kalkstickstoff, 1129
Kieserite, use for treating ammoniacal liquor, 1332
Kiton, 351, 367
Kreosteril, 811
Kresulfol, 810
Kyanol, 292

LAMPBLACK, 373, 610, 625; manufacture, 712; various qualities, 713; furnaces, 713; processes of working for soot, 715; improvements, 717; various apparatus, 718; dealing with the smoke issuing from the apparatus, 718; applications, 719; calcining apparatus, 720; properties, 722
  Manufacture from benzol, 1028
Lamps for creosote-oil, 666 (*see* this); for benzol and naphtha, 1017, 1019, 1021
Leucoline, 299
Lice, extermination by benzol, 1029
Light oil, production in distilling tar, 445, 854; properties, 854; composition, 855; applications as such, 856; for the manufacture of benzoic acid, 856; treatment with phosphoric acid, 857; working up the light oil, 857; distillation, 857; stills, 858; working the stills, 859; fractions, 860; English style, 861; French style, 862; German style, 863; yields of commercial products in working it up, 945; testing methods for it, 956; production from carbonaceous substances, 1588
Light-oil naphtha, 866 (*see* First runnings)
Lime, use for expelling the ammonia, 1336; preparation of milk-of-lime, 1339
Lime-mud from ammonia stills, 1491
Lime-nitrogen. *See* Calcium carbide and Cyanamide
Liming the coal in gas-making, 1200
Liquor ammoniæ. *See* Ammoniacal liquor
Locality for treating benzol and naphtha, 884, 1007
Lucigen lamp, 668
Lutidines, 296
Lymn gas-producer, 1223, 1225, 1227, 1228
Lymn gas washer, 1224
Lysoform, 661
Lysocresol, 661
Lysol, 660, 773, 1602
Lysopast, 813
Lysosulphol, 662

MACADAM pavement made with tar-varnishes, 559
Magnesia, use for driving out the ammonia from its salts, 1270, 1341
Magnesium nitride as catalyzer for the synthesis of ammonia, 1100
Massud, 191, 329
Mercaptans, 290
Mesitylene, 237
Metakalin, 810
Methane, 208
Methane series of hydrocarbons found in tar, 207
Methylanthracenes, 255, 640
Methylcumarones, 263
Methylethylketone, 266
Methylindenes, 243
Methylnaphthalenes, 246
Methylpyrrols, 305

Methylquinolines, 299, 300
Methylthiophen, 288
Microbes, action of benzol on, 1029
Microsol, 810
Middle oil, 449, 724 (*see* Carbolic oil); examination, 781
Mixing-vessels for carbolic oil and alkali, 738; for the chemical treatment of naphtha, 871
Molasses, recovery of ammonia in working it up, 1149
Mond gas-process, 1213, 1219, 1221, 1222
Montejus for tar-distillates, 431
Moor-lands, ammonia from, 1169
Motors and motor cars, driving by benzol, 1027
Moulds for the pitch, 478, 480

NAPHTHA (*see* Solvent-naphtha and Burning-naphtha), obtained by steam distillation of tar, 382; by distilling light oil, 861
  Complete separation into pure benzene, toluene, xylene, etc., 922; composition and properties of commercial naphtha, 948
  Practical tests for final products, 994, 998, 1000, 1004, 1005
  Pecuniary valuation, 1003
Naphthalene, 243; discovery, 243; formation, 243; properties, 243, 1596; removal from coal-gas by means of anthracene oil, 607; part played by it in the creosoting of timber, 694
  Obtaining it by cooling down carbolic oil, 729; from creosote oil, 651, 652; in various ways, 824
  Estimation in middle oils, 781
  Crude naphthalene, 824; purification, 825; cold and hot pressing, 826; other methods for removing the oils, 827, 1605; chemical purification of the pressed naphthalene, 828; by caustic-soda solution, 828; by sulphuric acid, 828; methods for preventing the reddening of naphthalene, 830; special processes for purifying naphthalene, 830
  Distillation of naphthalene, 832; danger of choking up, 833; safety-valves, 833; course of distillation, 834; applications of distilled naphthalene, 834; recrystallization, 835
  Moulding naphthalene into sticks, globes, powder, etc., 835; sublimation of naphthalene, 836
  Examination of naphthalene, 840; solidifying-point, 840; test for oil, 841; sulphuric-acid test, 841; test for constancy of colour, 841; for phenols, 841; for quinoline bases, 842; for other hydrocarbons, 842; qualitative test for naphthalene, 842; quantitative estimation, 842; by picric acid, 842, 1606
  Applications, 844; as fuel, 844; for the manufacture of colours, 844; for carburetting gas, 845; albo-carbon light, 845; similar apparatus, 847; for driving gas-motors, 848; as disinfectant and insect-killer, 849; combination with sulphur, 850; various other uses of naphthalene, 850, 1606; statistics, 852, 1606; removal from coal-gas, 1015
Naphthalene dihydride, 245
Naphthalene oil, 652
Naphthalene tetrahydride, 246
Naphthenes, 214, 239
Naphthofuran, 284
Naphthols, 279
Nigro-powder, 1030
Nitragin, 1048
Nitrating-test for crude benzol, 975
Nitre-beds, Chilian, exhaustion, 1048
Nitre-cake, use for the manufacture of ammonium sulphate, 1614
Nitric acid, manufacture from ammonia, 1332
Nitrides, production of ammonia from, 1095; use as catalyzers, 1095
Nitrogen, atmospheric, use for the production of ammonia, 1048, 1053; 1608
  Isolation by chemical processes, 1055, 1607, 1608; by physical methods, 1056; fractional distillation of liquefied air, 1057
  Manufacture of ammonia from it, and hydrogen or steam by means of catalyzers, 1065; laboratory investigations, 1065; process of Haber, 1070; his patents, 1075; patents of the Badische, 1076, 1079; other processes, 1085
  Percentage in coal, 1184; estimation, 1185
Nitrogen oxides and nitrate of soda, formation of ammonia from them, 1145
Nitrum, 1048
Nonane, 210
Nonone, 221, 222
Noxious vapours evolved in tar-distilling, 432, 477
Nuisance from ammonia-works, prevention of, 1489

OIL-GAS process, obtaining tar and tar-products in it, 105
Olefins, 21[illegible]
Oleic acid, use for washing crude anthracene, 615
Oleo-vapour lamp, 671
Oxybenzlampe, 1021
Oxychinaseptol, 809
Oxyphenols, 278

PALLADIUM as catalyzer for the synthesis of ammonia, 1087
Pantopollite, 851
Parachrysene, 262
Paraffenes, 214
Paraffin in coal-tar, 211; removal from crude anthracene, 614; estimation, 641, 649; in crude benzol and naphtha, 972; sulphonation method, 972
Paraffin oils, tar obtained by superheating them, 187; use for washing crude anthracene, 615
Paranthracene, 254, 255
Parvolines, 297
Patent-fuel (briquettes), 360; manufacture from pitch, 539; historical, 539; statistics, 540; raw material, 542; quality of the pitch for it, 542, 1600; properties of good briquettes, 544; briquette-moulding-machines (presses), 545, 1601; application of the pitch as dust, 1600; testing the quality of briquettes, 548
Peat, ammonia from it, 1168
Pentane, 209
Perkeo, 885
Petroleum oils, use in the end of tar-distillation, 470
Petroleum residues, tar obtained by superheating them, 187; burning as fuel, 329
Petroleum-spirit, use for washing crude anthracene, 612; discovery in crude benzol, 973
Phenanthrene, 256; recovery from solvent-naphtha, 611; preparation, 624; uses, 626; estimation, 643; discovery, 644
Phenanthrene hydrides, 258
Phenol, discovery, 266; occurrence and formation, 266; synthetical production, 267; properties, 268; specific gravities, 269; solubilities, 269; smell, 270; taste, 270; poisonous and coagulating action, 271; reddening, 271; reactions, 272; affinity to bases, 273; solubility in sulphuric acid, 273; action of nitric acid, 273; acidic properties, 1597
  Higher phenols in coal-tar, 278
  Commercial forms. *See* Carbolic acid
  Manufacture. *See* Carbolic acid
  Estimation of the phenols in carbolic oil, 782; of the solidifying-point, 782; in carbolic soap, etc., 815; in light oil, 957
  Phenol, commercial crude, 785; crystallized, 785
  Testing methods. *See* Carbolic acid
  Phenols in waste liquor from ammonia stills, 1493
Phenola, 606
Phenolith, 812
Phenopast, 813
Phenosalyl, 810
Phenostal, 811
Phenylmethylketone, 266
Phenylnaphthalenes, 247
Phenylnaphthylcarbazol, 307
Picene, 262
Picene hydrides, 263
Pickling timber by creosote oil (*see* this)
Picoline, 295, 904
Pintsch gas, tar from, 65
Pitch, manufacture from tar without distillation, 368; formation in the distillation, 451, 453; distilling soft to hard pitch in a special still, 453; running it off, 458; softening the pitch in the still, 469; by means of petroleum oils or other oils, 470; running off the hard pitch, 471 (*see* Pitch-bags, etc.); into moulds, 478, 480
  Nature of coal-tar pitch, 531; formation, 532; elementary composition, 532; solubility, 533, 535; general properties, hard and soft pitch, 534; specific gravity, 534; softening- and fusing-points, 534; elementary composition, 535; other properties of hard pitch, 536; grinding pitch, 1600
  Apparatus for pitch-revivifying (softening), 537; applications of pitch, 539; manufacture of patent fuel, 539 (*see* this)
  Purification by extraction with solvents, 563
  Distillation for coke, 564; pitch-ovens, 565; apparatus of Fenner and Versmann, 567; distillation for anthracene, 570; other processes, 571, 1601; quality of pitch-coke, 571; use of it for electric carbons, 572, 1602
  Use of pitch as reducing agent, 573; for various purposes, 573; for lamp-black, 573
  Disease caused by pitch (pitch-cancer), 574
  Testing of pitch, 575; estimation of specific gravity, 575; of free carbon, 575; of coking-residue, 576; of softening- or melting-point, 576; testing the consistency of bituminous binders in the asphalt-paving industry, 581; testing for viscosity, 582; estimation of the bituminous substances, 582; other tests of pitch, 584
  Distinction between coal-tar pitch and other descriptions of pitch and asphalt, 585; distinction from natural asphalt, 585
  Statistics on pitch, 588
Pitch-cancer, 201, 598
Pitch-bags, 474
Pitch-chambers, 472
Pitch-cooler, 472, 473

Pitch-holes, 474
Pitch-house, 472 ; explosions or fires in these, 475
Pitch-oven, 472
Poisonous properties of coal-tar, 314 ; of pitch, 574, 598
Potash, caustic, use for purification of crude anthracene, 618
Prepared tar, 549
Presses, for crude anthracene, 598 ; for naphthalene, 826
Pressure-regulator for naphtha stills, 331
Producer-gas, ammonia from, 1207, 1231, 1252
Products from coal-tar, synopsis, 1035
Propane, 209
Propylene, 212
Pseudocumene, 237
Pseudophenanthrene, 258
Pumping of coal-tar, 380
Pyrene, 259
Pyridine, 293 ; use for washing crude anthracene, 615 ; rules for the pyridine bases for denaturing spirit of wine, 902 ; in ammoniacal liquor, 1186
Pyridine bases from creosote oil, 654 ; from carbolic oil, 740 ; estimation in middle oil, 784 ; recovery from the chemicals used in washing naphtha, 876 ; from acid-tar, 895
  Distillation of crude pyridine, 899 ; isolation of the various bases, 899 ; recovery of pyridine bases from crude ammoniacal liquor, 900
  Purification of pyridine, 900
  Analytical methods for pyridine bases, 900 ; applications, 615, 903 ; estimation in commercial benzol, 988 ; in ammoniacal liquor, 1186
Pyridine series, 293, 904
Pyridine-sulphuric acid, 897
Pyrites-acid for sulphate of ammonia, 1465, 1466
Pyrocresols, 277
Pyrrol, 304

QUARRITE, 366
Quinaldines, 299
Quinoline, 299, 904
Quinoline series, 29[illegible]

RAILROAD sleepers, pickling them with creosote oil, 692
Receivers for tar-stills, 428 ; for ammoniacal vapours, 1382
Refined tar, 549, 1601 ; testing its quality, 550
Resinite, 814
Retene, 263
Revivifying hard pitch, 537
Rhodin, 852
Rhodium as catalyzer for the synthesis of ammonia, 1090
Roads, tarring of, 361
Roburite, 1030
Roofing-felt manufacture, 353
Röpert-Oel, 844
Rosin-oil emulsions with creosote oil, 662
Rosolic acid, 280 ; discovery, 280 ; formation, 280
Rubidine, 297
Ruthenium as catalyzer for the synthesis of ammonia, 1087, 1090

SAFETY-VALVE for tar-stills, 416, 448 ; for naphthalene-stills, 833 ; for ammonia-stills, 1343
Sal-ammoniac, historical notes on, 1041 ; properties, 1312 (*see* Ammonium chloride) ; manufacture (*see* Ammonium chloride)
Salubrin, 850
Samples for testing coal-tar, way of taking them, 520
Sanatolyse, 810
Sapocarbol, 658, 660
Sapophenol, 662
Saprol, 810
Saturation test for ammonia, 1268
Saturators for sulphate of ammonia, 1463 ; quality of the sulphuric acid, 1464, 1614 ; various forms of saturators, 1467 ; nuisance caused by the gases and vapours from them, 1496 ; combustion of the gases, 1497 ; utilization for producing sulphuric acid, 1499
Seeschlick, ammonia from, 1167
Sewage, recovery of ammonia from, 1154 ; working for sulphate of ammonia, 1458
Shale, recovering ammonia in its distillation, 1182
Shale-oil in crude benzol, testing for, 972
Silicon nitride for the production of ammonia, 1096
Soldering metals by means of benzol, 1029
Solidifying-point of crude phenol, methods for ascertaining it, 782
Solutol, 809
Solvent-naphtha, used for washing crude anthracene, 609 ; treatment of the used naphtha by redistilling, 610 ; obtaining it in fractionating crude benzol, 919 ; commercial qualities, 920 ; composition, 920 ; uses, 921
Solveol, 809
Soot, 373 ; manufacture (*see* Lampblack)
Sozal, 809
Sozojodol, 809
Specific gravities, tables for reducing to normal temperature, 1583 ; for comparing the degrees of various hydrometers, 1584

Specific gravities of tar-oils, reducing them to the ordinary temperature, 441; of tar, way of estimating it, 520; estimation of pitch for it, 575
Spent oxide of gas-works, ammonia from, 1206; estimation for ammonia, 1290
Spray producers for burning tar, 338; for burning creosote oil, 675
Standard acid for titrating ammonia, 1273
Steam, use for promoting the distillation of tar, 437; application of superheated steam in the last stage, 455; drying the steam, 457, 462, 568; use for increasing the yield of ammonia in gasifying coal, 1203, 1207
Steam-pipes for tar-stills, 418
Sterilizing by benzol, toluol, etc., 1029
Stills for tar (*see* Tar-stills); for naphthalene, 832; for light oil, 858; for crude benzol, 886; steam-stills for light naphtha, 907; English stills, 907; similar stills, 910; working the stills, 911; receivers, 913; fractionation, 914; self-acting control of it, 916; fractions obtained, 916; French process, 919
Stills for complete separation of naphtha into pure benzene, toluene, xylene, etc., Coupier's, 922; Vedlé's, 926; Savalle's, 927; Heckmann's, 934; various, 934; coolers, 935
Stills for ammonia, mode of heating them, 1342; safety-valves, 1343; waste liquor and lime mud, nuisance 1491
Stockholm tar, artificial, 549
Store-tanks for coal-tar, 378; for tar distillates, 430; for benzol and naphtha, 1007, 1009; of ammoniacal liquor, 1329
Street-pavements made with tar-asphalt, 556
Stupp, 252
Styrolene, 239
Sublimation of anthracene, 622; of naphthalene, 836
Succisterene, 262
Suffioni, 1051
Sulphite, absorption of ammonia as such, 1480
Sulphocyanide. *See* Thiocyanate
Sulphonating-test for creosote oil, 706
Sulphur, free, in coal-tar, 290; production from ammonia-saturator gases by the Claus process, 1500
Sulphur compounds in coal-tar, 285; removal from benzol, 936; estimation of total sulphur in benzol, 987
Sulphur dioxide, recovering ammonia by means of it, 1238; absorption of ammonia by it, 1480
Sulphur-dioxide, liquid, for washing crude anthracene, 616
Sulphur-tar, 372
Sulphuretted hydrogen for decomposing sodium phenylate, 749
Sulphuric acid for washing the naphtha, 869, 876; action of the acid, 869; waste acid (*see* Acid-tar); for sulphate of ammonia, 1464; brimstone acid, 1465; pyrites acid, 1465; concentration, 1466; quantity, 1467; production from saturator gases, 1499
Superheated steam, application in the last stage of tar-distilling, 455; way of producing it, 456, 458
Superheated water, distillation of tar by it, 454
Superheating oils and vapours, obtaining tar and tar-products by it, 185
Synanthrene, 258

TANK-WAGONS for coal-tar, 376
Tar, production in the destructive distillation of coal, 13; constituents of tar from peat, browncoal, and bituminous shale, 13
Tar produced from coal, 14; hydrocarbons contained in it, 15; conditions for the formation of aromatic and aliphatic hydrocarbons, 15; water-gas tar, 16
  Historical notes on the application of coal-tar and the products obtained therefrom, 16
  General observations on the use of coal-tar for industrial purposes, 21; market prices of coal-tar and tar-products in former times, 22; decline of prices, 23; present state of affairs, 26
  Quantity of coal-tar produced, 27; older statistics, 28; recent statistics, 29; for the United Kingdom, 31; for the United States, 32; for various countries, 33; for Germany, 34; present state, 36
Tar, production at gas-works, 37 (*see* Gas-tar); recovery of the tar suspended in the gas, 56, 1587, 1588, 1591; estimation of the tar contained in gases, 62
  Production by superheating certain oils and vapours, 185
  General observations on coal-tar from various sources, 196
  Determination of the yield of tar and ammonia from coal, 198

  Properties of coal-tar and its constituents, 200; specific gravity, 200; poisonous action, 200
  Composition, 201; ultimate analysis, 201; enumeration of the compounds contained in coal-tar, 202
Tar, applications without distillation, 315; historical notes, 315; in the manufacture of illuminating-gas, 316; burning as fuel, 322, 1597; comparison of its calorific

[illegible] with coke, 344; burning for motive power, 348; for heating coke-ovens, 349; application for preserving stones, brickwork, etc., 349; for painting metals, 351; for preserving wood, 352; for the manufacture of roofing-felt, 353, 1597; as cementing substance, 360; for patent fuel (briquettes), 360; for making and improving roads, 361, 1597; for making asphalt and pitch without distillation, 368; for antiseptic and medicinal purposes, 371; for denaturing alcohol, 373; for producing coke, 373
  Distillation (*see* this)
  Carriage in boats, 376; in trucks, 376; store-tanks, 378; wells, 379; explosions in reservoirs, 380; pumping into stills, 380; dehydration, 384, 1597
Tar, "prepared" or "distilled" (artificial Stockholm tar). *See* Varnishes
Tar, testing in the laboratory, 513; method of Watson Smith, 513; of Lunge, 515; of Rispler, 519; other ways, 519; taking samples for testing, 520; testing for specific gravity, 520; estimation of water, 522; of free carbon, 523; of coking-residue, volatile substances, ashes, 526; of viscosity, 526
Tar-acids, testing for, [illegible]05
Tar-fog, removal from the gases before treating them for ammonia, 1335, 1598
"Tar-mac" process, 366
Tar-separators, 385, 386
Tar-distillation, consumption of fuel, 501
Tar-distillation yields, 502; from English tars, 503; from German tars, 508
Tar-oils used in the construction of basic linings in steel-works, 608
Tar-stills, wrought-iron as material for them, 397; corrosion of the iron, 398; curtain-arches, 398; thickness of the plate, 399; best shape of tar-stills, 399; upright cylinders, 400; testing the tightness, 400; joints, 403; English stills, 403, 404; horizontal cylinders, 405; special forms of stills, 405, 1599; wagon-shaped stills, 406; stills with mechanical agitators, 408; detailed description of a tar-still and the auxiliary apparatus belonging to it, 410; (shape, 410; fire-place, 412; steam-pipe, 414; fire-flues, 414; mountings, 415; supply-pipe, 415; tap for running off the pitch, 415; still-head, 41[illegible]; manhole, 416; safety-valve, 416; thermometer, 417; precautions for fixing pipes and mountings, 418; steam pipe, 418); setting the still, 41[illegible]; condensing apparatus, 421 (*see* this)
Tar-stills, working them, 436; charging, [illegible]; heating up, 437; preventing the boiling over, 437, 438; signs of the beginning of the distillation, 438; agents promoting the boiling over, 438; breaking up the froth, 438; fractions, 440 (*see* this); explosions, 447; end of the distillation, 451, 468
  Distillation by means of superheated water, 454; by superheated steam in the last stage of the process, 455; Kubierschky's process for distilling tar by superheated steam in columns, 458, 1599
  Mechanical agitators in tar stills, 459
  Distillation in a current of inert gases, 463; in a vacuum, 464, 1599; running off the pitch, 468 (*see* this)
  Time required for working off the tar stills, 499
Tar-stills, continuously working apparatus, 481; (Mallet, 481; Vohl, 481; various, 483; Lennard, 483; Mason, 487; Propfe, 488; Hirzel, 490; Köhn, 491; Ray, 493; Kubierschky, 494; various, 494); opinion of experts on this system, 495, 1599
  Working-capacity of a tar-distilling plant, 512
Tar-tester (Lunge's), 550
Tarry substances, removal from ammonia gas, 1366; in ammoniacal liquor, 1385
Tetramethylbenzenes, 938
Tetramethylthiophen, 289
Thelen-pans, 1488
Theory of the formation of the constituents of coal[illegible], 309
Thermometers for fractional distillation, 968; table for comparing the Centigrade and Fahrenheit degrees, 1585
Thiocyanate, determination, 1279, 1282; recovery from the waste liquor of ammonia-stills, 1494; impurity in sulphate of ammonia, 1206, 13[illegible]9, 1516
Thiophen, discovery, 286; preparation, 286; properties, 287; in benzol, 937; removal, 938; estimation, 984
Thiophen derivatives, 289
Thiosulphate, determination, 1280, 1281
Thiotolen, 288
Thioxen, 288
Timber, pickling by creosote oil (*see* this)
Titanium as catalyzer for the synthesis of ammonia, 1088; titanium nitride as catalyzer for the synthesis of ammonia, 1097
Titanium cyano-nitride for the preparation of ammonia, 1143
Toluene, recovery from coal-gas, 81, 1589, 1593; discovery, 23[illegible]; properties, [illegible]; determination in commercial products, 970, 992, 993, 1607; from Borneo petroleum, 1594, 1595; production by synthesis, 1607

Toluol, commercial, 918; impurities, 940; conversion into pure toluene, 941
Toluene, pure, requirements for, 955-6
Trimethylbenzenes, 236; estimation, 923
Trimethylthiophen, 289
Trotyle, 1030
Truxene, 261
Turbinenmischer, 875

UNDECANE, 211
Urea, synthetical, 1519
Urine, ammonia from, 1052, 1154

VACUUM, application in tar-stills, 461
Valylene, 220
Vanadium as catalyzer for the synthesis of ammonia, 1088
Vapours evolved in the distillation of tar, 432, 439, 479
Varnishes made with pitch, 548; preparation, 548; testing for viscosity, 550; for volatile constituents, 552; for their quality as protectors of iron against rusting, 552; better kinds of varnishes, 553; special methods, 554 (*cf.* asphalt)
Vigorite, 1030
Vinasse, recovery of ammonia from, 1149
Viscosity of coal-tar, estimation, 526, 550; of pitch, 582
Viridine, 298
Vitriol-tar, 887, 1466
Volcanoes, ammonia from, 1051

WASHING, [illegible] 869; with sulphuric [illegible] alkali, 87[illegible], 879; with [illegible] of vitriol, 882 (*see* [illegible])
Waste liquor from [illegible] prevention of nuisance by [illegible] bacterial treatment, 1493
Water contained in coal-tar, [illegible]; separation from tar by settling, 384; by centrifugalling, 386; by heat, [illegible]; by chemical methods, 393
Estimation of water in coal-tar, [illegible]
Water-gas, obtaining tar in its manufacture, 179; composition, 181; working it up, 184
Wells for coal-tar, 379
Westrumite, 662
Wood, painting with coal-tar, 352
Wood-cement, 352, 560

XANTHENE, 285
Xanthogenate method for estimating carbon disulphide, 982
Xenols, 278
Xylenes (xylol), 234; preparation in the pure state, 942; separation of the isomeric xylenes, 943; determining their quantity in commercial xylol, 992
Xylenols, 278

ZINC as catalyzer for the synthesis of ammonia, 1087
Zinc chloride, mixtures with creosote oil, 657

CONTENTS

PART III

CHAPTER XII

HISTORICAL NOTES ON AMMONIA—RISE AND FUTURE OF THE INDUSTRY OF AMMONIA

PAGE
Historical Notes on Ammonia and its Compounds 1041
First mention of sal-ammoniac . 1041
of ammonium carbonate and free ammonia 1043
of ammonium sulphate . . 1045
Historical Notes on Ammonia and its Compounds—continued.
Former applications of ammonia . 1045
First industrial production . . 1046
Further development of this industry 1048
Its future 1049

CHAPTER XIII

SOURCES FROM WHICH AMMONIA IS OBTAINED

Natural occurrence of Ammonia . . 1050
Guano 1050
Suffioni 1051
Volcanoes 1051
Carnallite 1051
Formation of Ammonia by putrefaction 1052
by nascent hydrogen . . . 1053
from cyanogen compounds . 1053
by the decay of nitrogenous organic substances . . 1054
by destructive distillation . . 1054
Synthetical Production of Ammonia from Nitrogen and Hydrogen . 1054
Separation of nitrogen from atmospheric air 1055
by chemical processes . . 1055
by physical methods . . . 1056
Synthetical Production of Ammonia from Nitrogen and Hydrogen—contd.
Preparation of hydrogen . . 1059
Production of a mixture of nitrogen and hydrogen . . . 1064
Manufacture of ammonia from free nitrogen by high temperatures, with or without the aid of catalytic agents (except by the aid of electricity) 1065
Various processes . . . 1065
Process of Haber . . . 1070
of the Badische Anilin- und Sodafabrik . . . 1076
Further processes for the synthesis of ammonia from its elements by various catalyzers . . 10[illegible]

Synthetical Production of Ammonia from Nitrogen and Hydrogen—contd.

PAGE
Synthesis of ammonia from nitrogen and hydrogen by the aid of the electric current . . 1090
Production of ammonia from free nitrogen by the *intervention of nitrides* 1095
  Boron nitride 1095
  Silicon nitride 1096
  Titanium nitride . . . 1098
  Magnesium nitride . . . 1100
  Calcium nitride. . . . 1102
  Aluminium nitride . . . 1102
  Serpek's process . . . 1102
  Other processes. . . . 1110
  Ferric or ferro-aluminium nitride 1112
  Various nitrides. . . . 1112
By the intervention of cyanides . 1113
  By barium cyanide . . . 1114
  Mond's process 1115
  Other processes. . . . 1118
  By various cyanides . . . 1119
Calcium Carbide and Cyanamide (lime-nitrogen and nitrolime) 1123
  Historical notes, laboratory investigations . . . 1123
  Pure calcium carbide. . . 1125
Technical processes for the preparation of calcium carbide and cyanamide (lime-nitrogen) . 1127
  Processes of Frank and Caro . 1128
  Other processes. . . . 1131
Uses of calcium cyanamide . . 1137
Production of ammonia from calcium cyanamide . . . 1137
  Manufacture of graphite . . 1140
  Storage of calcium cyanamide . 1140
  of cyanides from lime-nitrogen 1140
  Statistical notes on the industry of calcium cyanamide. . 1140
Analytical methods for cyanamides 1142
Ammonia prepared by means of titanium cyanonitride . . 1143
Ammonia formed from *nitrogen oxides* and in *various inorganic chemical* processes . . . 1145

PAGE
Ammonia as a by-product in the manufacture of beetroot sugar (molasses, vinasse) . . . 1148
Ammonia from urine, sewage, etc. . 1154
Ammonia from guano . . . 1161
Ammonia from bones, horn, leather, wool, hair, and other animal substances 1162
Ammonia from peat. . . . 1168
  Process of Frank and Caro . . 1179
Ammonia from bituminous shale . 1182
Ammonia from coal 1184
    Percentage of nitrogen in coal . 1184
  Production of ammonia in the manufacture of coal-gas and coke 1185
    Yield of ammonia in the manufacture of coal-gas . . 1187
  Special processes for the treatment of coal-gas for ammonia. . 1193
    Feld's processes . . . 1196
    Burkheiser's process . . . 1199
  Processes for increasing the yield of ammonia in gas-making . 1200
    by lime 1200
    by hydrogen 1202
    by steam 1203
  Ammonia, etc., recovered from coal-gas directly, without scrubbers 1204
Ammonia from the spent oxide and other by-products of gas-works . 1206
  From calcium-carbonate mud . 1207
Production of ammonia by treating coal or shale with steam (producer-gas, Mond gas) . . 1207
    Process of Young and Beilby. 1208
    Other processes . . . 1212
  The Mond gas-process . . . 1213
  The Lymn gas-producer . . 1223
  Ammonia from other gasifying processes 1231
Ammonia from coke-ovens . . 1234
  Direct sulphate processes . . 1236
  Recent improvements in the recovery of ammonia from coke-oven gases 1237
  Recovery of ammonia by means of sulphur dioxide and conversion of the sulphite into sulphate . 1238

PAGE
Ammonia from coke-ovens—*contd.*
Condensing-apparatus for the ammonia from coke-oven gases . 1240
Statistics on the production of ammonia from coke-ovens . . 1244

PAGE
Ammonia from blast-furnace gases . 1245
Ammonia from producer-gas . . 1252
Ammonia from the ordinary products of combustion (coal-smoke) . 1254

CHAPTER XIV

THE COMPOSITION AND ANALYSIS OF AMMONIACAL LIQUOR, AND PROPERTIES OF ITS CONSTITUENTS

General 1256
Composition of Ammoniacal Liquor . 1256
"Fixed" and "volatile" ammonia 1256
Influence on the composition of the gas-liquor exerted by the style of the retorts 1258
by the washing-out of the cyanides from the gas . . . 1258
by the oxidizing action of the air 1259
Cox's tables showing the composition of gas-liquor from different points in the condensing- and scrubbing-plant 1260
Distribution of sulphur and cyanogen in ammoniacal liquors from various sources . . 1263
Ammonium salts in recovered sulphur from Claus-kilns . 1264
Analyses of gas-liquor by Mayer and Hempel 1264
Valuation of Ammoniacal Liquor . 1266
by the hydrometer . . . 1266
by chemical methods . . . 1266
1. Estimation of the volatile ammonia 1267
2. Estimation of total ammonia—
(*a*) Methods for the use of workmen 1269
(*b*) Accurate method (distillation test) . . . 1270
(*c*) Azotometric test . . . 1274
Valuation of Ammoniacal Liquor—continued.
Complete analysis of ammoniacal liquor 1277
Methods of Dyson . . . 1277
of the Alkali Inspectors (Linder) . . . 1281
of Mayer and Hempel . 1283
Special methods for sulphides, cyanides, phenols, etc. . . 1284
for pyridine bases . . 1286
Examination of *concentrated ammoniacal liquor* 1289
Estimation of ammonia in *spent oxide of gas-works* . . . 1290
Properties of Ammonia and its technically important Salts . . . 1291
Ammonia 1291
Dry ammonia 1291
Physical properties of gaseous ammonia 1292
Properties of anhydrous liquid ammonia 1292
Specific gravity at various temperatures 1293
Specific heat 1293
Cold produced by the evaporation of liquid ammonia . 1294
Electric conductivity . . . 1294
Solvent powers 1294
Metal-ammonium compounds . 1294
Behaviour of ammonia to water . 1295
Dissolving-heats . . . 1295
Absorption by water at various temperatures and pressures . 1296

PAGE
Properties of Ammonia and its technically important Salts—continued.
Specific gravities of aqueous solutions of ammonia . . . 1297
Hydrates of ammonia . . 1298
Vapour-pressures of aqueous solutions of ammonia . . 1298
Solubility of ammonia in solutions of salts, etc. 1299
in alcohol 1299
Absorption of ammonia by solid substances (wood, charcoal, and others) 1300
Chemical behaviour of dry ammonia . 1301
Decomposition by the electric current 1301
by heat 1301
by light 1304
by radium emanation . . 1304
Combustibility 1304
Behaviour towards various elements and oxides . . 1305
towards other gases and liquids 1306
Physiological properties . . 1307
Chemical behaviour of *aqueous solutions of ammonia* (liquor ammoniae) 1307
against electricity . . . 1308
against sulphur, chlorine, hydrogen sulphide, salts . 1308
against anhydrous acids . . 1309
against carbon disulphide . 1309

PAGE
Properties of Ammonia and its technically important Salts—continued.
Ammonium *sulphides* . . . 1310
sulphocyanide (thiocyanate) . . 1310
cyanide 1311
ferrocyanide 1311
chloride (sal-ammoniac) . . 1312
fluoride 1314
carbonates 1315
Solutions of carbonate of ammonia 1318
Ammonium *sulphates* . . . 1319
sulphites 1321
thiosulphate 1321
persulphate 1321
nitrite 1322
nitrate 1322
phosphates 1324
chromates 1324
chlorate 1324
perchlorate 1325
formate 1325
acetates 1325
oxalates 1325

CHAPTER XV

THE WORKING-UP OF AMMONIACAL LIQUOR INTO CONCENTRATED LIQUOR AND PURE AMMONIA

Storing and separating from Tar . 1326
Working-up without distillation—
Direct saturation without acids . 1329
Treatment with calcium or magnesium sulphate, etc. . . 1330
Oxidizing the ammonia into nitric acid 1332
Removal of the *cyanides* from gas-liquor before distillation . . 1333
Removal of *tar-fog* from the gases . 1335
Manufacture of ammoniacal compounds by *distilling* the liquor . 1336
Question of boiling with or without *lime* (volatile and fixed ammonia) 1336
Preparation of the *milk-of-lime* . 1339
Use of other compounds for liberating the ammonia (magnesia, etc.) 1341

Manufacture of ammoniacal compounds—*continued.*

PAGE
Mode of heating the stills . . 1342
Safety-valves 1343
Various products made from gas-liquor 1343

Manufacture of Concentrated Gas-liquor 1344
for moderately concentrated liquor 1344
for higher concentrations . 1345
Apparatus of Solvay . . . 1345
of Grüneberg for direct firing. 1347
Grüneberg and Blum's steam-still. 1351
Apparatus of the Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft ("Bamag"). . . 1351
Other apparatus 1358
Special processes for treating ammoniacal liquor . . . 1358
Concluding remarks . . . 1359

. *Manufacture of Pure Liquor Ammoniæ* 1360
Former processes . . . 1360
Addition of lime . . . 1360
Consumption of steam . . 1360
Removal of hydrogen sulphide and carbon dioxide without lime . 1361
Various processes . . . 1361
Process of Solvay . . . 1362
of Julius Pintsch Aktien-Gesellschaft . . 1365
Purification of the ammonia gas from empyreumatic (tarry) substances 1366
Apparatus for the manufacture of pure liquor ammoniæ . . 1368
Simple apparatus with a directly-fixed still 1368
Apparatus of Elvers and Pack . 1370
Apparatus of the Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft ("Bamag") . 1373
of Hirzel 1374
of Feldmann 1375
of Mallet 1375
Various apparatus . . . 1377

II. *Manufacture of Pure Liquor Ammoniæ*—continued.

PAGE
Absorption of the ammonia vapours in water 1380
Coolers 1381
Receivers 1382
"Solid Ammonia" . . . 1383
Absorption by hygroscopic salts . 1383
Carriage and storage of liquor ammoniæ 1383
Uses of liquor ammoniæ . . 1385
Testing of liquor ammoniæ . . 1385
Tests for pyridine . . . 1386
Other tests 1386

III. *Manufacture of Anhydrous Liquid Ammonia* 1388
Historical notes 1388
General principles . . . 1389
Purification of the gaseous ammonia before compression . 1390
Removing the moisture . . 1390
Testing the ammonia gas for moisture 1391
Intermediate vessels for the gaseous ammonia 1393
Compressors for liquefying ammonia gas 1394
Cooling of the compressed gas (intermediate coolers and condensers). . . . 1395
Combination of apparatus for the manufacture of liquid ammonia. 1396
Apparatus of the Germania Engineering Works . . . 1396
of the Maschinenfabrik Sürth 1399
of Teichmann . . . 1400
Various processes for making liquid ammonia 1403
Storage and carriage of liquid ammonia 1404
Properties of commercial liquid ammonia 1408
Applications of liquid ammonia . 1409
Analysis of liquid ammonia . . 1410

CHAPTER XVI

MANUFACTURE OF SULPHATE OF AMMONIA

PAGE

- Older processes 1414
- Manufacture by distilling the ammonia into receivers containing sulphuric acid 1415
  - Apparatus for this purpose . . 1415
- Coffey still 1416
- Horizontal cylindrical stills . . 1423
- Continuous saturation apparatus . 1424
- Dutch apparatus 1426
- Apparatus of Mallet 1427
  - of Grüneberg 1432
  - of Grüneberg and Blum . . 1435
  - of Feldmann 1439
  - of Julius Pintsch 1443
  - of Heinrich Hirzel 1443
  - of P. Mallet 1446
- Various forms of ammonia-stills . 1447
- Obtaining ammonium sulphate free from cyanides 1450
- Treatment of ammoniacal liquor in the cold state for removing hydrogen sulphide and carbon dioxide 1454
- Apparatus specially intended for working sewage 1458
  - of P. Mallet, for treating thick sewage 1458
  - of Lencauchez 1460
  - Other apparatus 1463
- Arrangements for absorbing the vapours in sulphuric acid . . 1463
- Sulphuric acid for absorbing the ammonia 1464
  - Use of pyrites-acid . . . 1465
  - of acid-tar 1466
- Saturators 1467
- Absorption of ammonia as sulphite . 1480
- Other ways of producing sulphate of ammonia 1483
- Coloration of the ammonia sulphate, and means for avoiding it . . 1485

PAGE

- Treatment of the sulphate taken out of the saturator 1487

Prevention of Nuisance from Ammonia Works 1489

1. The reception, transportation, and storage of the ammoniacal liquor 1489
2. Leakages about the apparatus . 1490
3. Treatment of the condensed water 1490
4. Waste liquor and lime-mud from the stills 1491
   - Bacterial treatment of the liquor 1493
   - Recovery of sulphocyanide (thiocyanate) and ferrocyanide . 1494
5. Gases and vapours given off in the saturator . . . 1496
   - Damage to health . . . 1496
   - Discharging them into a chimney-shaft 1497
   - Combustion of the gases . . 1497
   - Utilising the SO_2 to produce sulphuric acid 1499
     - to produce sulphur in the free state 1500
   - The Claus process . . . 150[illegible]
   - Absorption of the combustion-gases by calcium carbonate. 1503
   - Other processes. 1505
   - Recovery of pyridine from the saturator-gases 1506
   - Absorbing the hydrogen sulphide in a purifier charged with calcium carbonate or oxide of iron 1507
   - Comparison of the results obtained by various processes. 1509

Concentration of Ammonium Sulphate Solutions 1511

- Smell arising from the evaporation of the sulphate liquors . . 1512

PAGE

Manufacturing Sulphate of Ammonia otherwise than from Ammoniacal Liquor 1512
Examination of Commercial Sulphate of Ammonia 1513
Percentage of ammonia . . 1513
Table for comparing the percentage of nitrogen and that of ammonia 1514
Moisture 1514
Free acid 1514
Colour 1514
Sulphocyanide 1516
Organic compounds injurious to plant life 1517

PAGE

Manufacturing Sulphate of Ammonia otherwise than from Ammoniacal Liquor—continued.
Prescriptions laid down in sale-notes for sulphate of ammonia 1517
Applications of sulphate of ammonia 1518
Statistics 1520
Great Britain 1520
United States 1522
Germany 1523
Italy 1524
Austria-Hungary . . . 1524
France 1525
Belgium and Holland . . 1525
World's production . . . 1525

CHAPTER XVII

OTHER TECHNICALLY IMPORTANT AMMONIUM SALTS

Ammonium Chloride (Sal-ammoniac) 1526
Historical 1526
Manufacture from camels' dung, etc. 1526
Manufacture by direct saturation of gas-liquor with hydrochloric acid 1527
Manufacture from the sulphate . 1530
Other processes. 1532
Properties of crude ammonium chloride. 1538
Purification of ammonium chloride by sublimation . . . 1539
Pure crystallized salt (muriate of ammonia) 1543
Purification from iron . . . 1544
Uses of ammonium chloride . . 1544
Statistics 1545
Ammonium Bromide 1545
Ammonium Fluoride 1546
Ammonium Ferrocyanide . . . 1547
Ammonium Sulphocyanide (Thiocyanate) 1547
from ammoniacal gas-liquor . 1547
from spent oxide of the purifiers 1548
Synthetical production from ammonia and carbon disulphide. 1550
Applications 1551
Analysis 1551

Ammonium Carbonates . . . 1552
Composition 1552
Formation in the destructive distillation of animal matters. . 1552
Manufacture from ammonium sulphate and calcium carbonate . 1553
Resublimation 1554
Drying 1555
Other methods 1556
Treatment of the calcium-carbonate mud 1559
Properties 1560
Applications 1560
Statistics 1560
Ammonium Nitrite 1561
Ammonium Nitrate 1561
Various methods for producing it 1562
Production from liquor ammoniæ and nitric acid . . . 1562
double decomposition of ammonium salts with nitrates . 1563
by oxidation of ammonia . . 1571
Various methods 1572
Statistics 1573
Preparation of granular ammonium nitrate 1573
Examination. 1573
Ammonium Persulphate . . . 1574

PAGE
Ammonium Perchlorate 1576
Ammonium Perborate 1577
Ammonium Thiosulphate . . . 1578
Ammonium Phosphates 1578
Ammonium Chromates 1580
Ammonium Formate 1581
Ammonium Acetate 1581
Ammonium Oxalate 1582

APPENDIX

Tables for reducing the specific gravities of liquids lighter than water to the normal temperature 1583
Table for comparing the degrees of Baumé's, Cartier's, and Beck's hydrometers with the corresponding specific gravities, for liquids lighter than water 1584
Table for comparing the degrees of the Centigrade and Fahrenheit thermometers 1585

ADDENDA

(Publications made during the printing of this Treatise.)

PAGE PAGE
13. The treatment of coal to obtain oils, ammonia, and other products 1587
54. Production of liquid hydrocarbons from coal . . . 1587
60. Tar-separators 1587
61. Removing the tar from coal-gas or producer-gas by a high-tension alternating electric current 1588
62. Production of light oils from carbonaceous substances . 1588
70. Recovery of benzene from illuminating-gas 1589
81. Recovery of toluene from coal-gas 1589
87. Determination of benzol in gas 1590
95. Statistics on coke-ovens fitted with recuperation plant . 1590
95. Statistics on the recovery of tar and ammonia from coke-ovens in the United States . 1591
98. Recovering tar and ammonia in carbonizing coal, etc. . 1591
137. Removing tar and ammonia from gases 1591
138. By-product coke-ovens . . 1592
157. Recovery of benzene, toluene, etc., from coke-oven gas . 1593
167. Recovery of by-products from coke-ovens 1593
184. Recovery of toluene in the manufacture of carburetted water-gas 1593
184. Production of benzene, toluene, xylenes, from Borneo petroleum oil 1594
194. Benzol and toluol from petroleum by the Rittman process 1594
194. Production of motor-spirit, benzol, and toluol from crude petroleum or petroleum by-product oils 1595
228. Properties of benzol from coke-oven gas 1596
231. Differentiation of coal-tar benzene (benzol) from petroleum benzene 1596
243. The vapour-pressures of naphthalene 1596
255. Solubility of naphthalene in ammonia 1596

PAGE PAGE
275. Acidic properties of alkyl-substituted phenols . . . 1597
344. Fuel efficiency of tar . . . 1597
360. Application of coal-tar for impregnating paper . . . 1597
360. Production of a binding material for coatings, etc., from coal-tar 1597
368. Tarring macadam pavement . 1597
371. Treatment of coal-tar . . . 1598
385. Removing tar from hot distillation gases 1598
392. Dehydration of tar 1598
393. Purification of coal-tar by treating it with oxygen . 1598
396. Preliminary treatment of raw tar before distillation . . 1599
408, 409. Tar-stills 1599
468. Distillation of tar under vacuum 1599
494. Tar-stills 1599
535. Machinery for grinding and loading hard pitch . . 1600
547. Manufacture of briquettes (patent fuel) . . . 1600
549. Refined tar 1601
555. Distinguishing natural and artificial asphalts . . 1601
562. Use of asphalt for coating stones. 1601
563. Utilization of pitch. . . . 1601
572. Carbon powder obtained from pitch 1602
660. Lysol 1602
688. Pickling timber . . . 1602
725. Manufacture of carbolic oil . 1602
765. Synthetical production of carbolic acid 1605
786. Quality of creosote for impregnating wood pavement . 1605
823. Carbolic acid statistics . . 1605
830. Purification of crude naphthalene 1605
843. Estimation of naphthalene by picric acid 1606
852. Applications of naphthalene . 1606
852. Statistics for naphthalene . 1607
893. Utilization of acid-tar from the purification of benzol . . 1607
942. Synthetical toluene . . . 1607
970. Analysis of commercial benzols 1607

PAGE PAGE
971. Determination of toluene . 1607
1027. Use of benzol for driving motor-cars 1607
1030. Statistics of benzol . . . 1607
1055. Preparation of nitrogen . . 1607
1059. Processes for the isolation of nitrogen from atmospheric air 1608
1060. Preparation of hydrogen . . 1608
1061. Production of ammonia from the elements by means of catalyzers 1609
1064. Carriage of liquefied hydrogen 1609
1087. Synthesis of ammonia by nitrides 1610
1088. Synthesis of ammonia . . 1610
1094. Synthesis of ammonia . . 1610
1096. Preparation of boron nitride . 1610
1109. Synthesis of ammonia by means of aluminium nitride . . 1610
1112. Beryllium nitride . . . 1610
1125. Behaviour of calcium cyanamide 1611
1136. Ammonia from cyanamide . 1611
1137. Injurious effects of the manufacture of lime-nitrogen on health 1611
1137. Preparation of calcium cyanamide (lime-nitrogen) . . 1611
1145. Synthetical production of ammonia. 1612
1153. Ammonia as a by-product in the manufacture of beetroot sugar 1612
1153. Ammonia from distillers' washes 1612
1182. Ammonia from peat . . 1612
1204. Recovery of ammonia from coal-gas washing-water . 1612
1213. Influence of steam on the yield of ammonia in gasifying coal or shale . . . 1613
1231. Ammoniacal liquor from tar by treating it with hot air . 1613
1234. Statistics on the recovery of ammonia in carbonizing coal 1613
1252. Ammonia from crude heating and lighting gases . . 1613
1264. Composition of gas-liquor from vertical retorts . . 1613

PAGE PAGE
1301. Properties of ammonia . . 1614
1329. Storage of ammoniacal liquor. 1614
1358. Manufacture of liquor ammoniæ 1614
1467. Use of nitre-cake in the manufacture of sulphate of ammonia 1614
1484. Ammonium sulphate . . 1614
1520. Statistics on sulphate of ammonia 1614
1532. Preparation of ammonium chloride by the action of sulphuric acid and ammonia upon alkaline chlorides . 1615

ALPHABETICAL INDEX OF NAMES . 1617

ALPHABETICAL INDEX OF SUBJECTS 1643

PART III

AMMONIA

CHAPTER XVII

OTHER TECHNICALLY IMPORTANT AMMONIUM SALTS

AMMONIUM CHLORIDE (SAL-AMMONIAC).

Properties, supra, p. 1312.—This salt formerly came from Egypt, and from the thirteenth century till late into the eighteenth this was the only source of ammonium salts available in Europe (apart from the use of putrefied urine in dyeing, etc.). In Egypt sal-ammoniac was made as a by-product in utilizing dried camels' dung for fuel. The food of the camels to a great extent consists of plants containing a large amount of salt, and their urine contains some ammonium chloride ready formed. The principal portion is, however, only produced from the nitrogenous substances and the chlorides when burning the camels' dung dried in the sun. The soot formed in burning was carefully collected and subjected to sublimation in special factories (one of which, in the delta of the Nile, was visited by the Jesuit Sicard in 1720). Forty lb. of soot are said to have yielded about 6 lb. of sal-ammoniac.

In other countries, where dried dung is also used as fuel, it has been sometimes attempted to manufacture sal-ammoniac by mixing common salt with the dung before burning it, and collecting the soot. This manufacture does not, however, seem ever to have had any considerable extension, except in India, whence large quantities of sal-ammoniac were formerly exported.[1]

In Europe sal-ammoniac is said to have been first obtained by the destructive distillation of oil-cake (a remarkably wasteful process!) and from the soot formed in the burning of coal.

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[1] A detailed account of the manufacturing processes formerly used in Egypt and India for making sal-ammoniac is contained in *Chemistry as applied to the Arts and Manufactures*, London (Mackenzie), i., p. 188.

The first sal-ammoniac factory in Germany was that of the brothers Gravenhorst at Brunswick, founded in 1759. In Scotland it seems to have been first manufactured about 1750, in France by Baumé.

The present manufacture of ammonium chloride is carried on in various ways—either by direct saturation of gas-liquor or similar ammoniacal liquids (*e.g.*, from the manufacture of bone-charcoal, or from putrefying urine) with hydrochloric acid, or by decomposing ammonium sulphate with sodium chloride, or by passing ammonia vapour into hydrochloric acid.

At some English works sal-ammoniac is still made by *direct saturation of gas-liquor with hydrochloric acid*, mechanically agitated. The escaping noxious gases are conveyed into the boiler-fire and burned. The faintly acid solution is left to settle; in three or four days the tar has separated out at the bottom of the vessel. Sometimes it is necessary to pass the liquid through canvas filters. The solution of ammonium chloride, still dark brown, is evaporated by direct fire in iron pans, and is always kept neutral or faintly alkaline by means of a little lime, chalk, or ammoniacal liquor. During the evaporation tarry oils are again separated, and are skimmed off along with a little ferric oxide. The vapours ought to be condensed, as they cause a considerable nuisance. When the liquor has attained the required strength, it is run into tubs 8 ft. wide and 2½ ft. deep, where the crystallization is finished in eight or ten days. Every six or eight hours it is stirred up in order to get small crystals, which are better for subliming. Finally, the mother-liquor is run off by a plug-hole in the bottom, which is best made to slope to one side. This way of proceeding requires an excessive quantity of fuel for concentrating the weak liquor.

More rational is the plan nowadays followed, where the *concentrated* solution of ammonium carbonate and sulphide, obtained by one of the apparatus described in Chapter XV., is mixed with hydrochloric acid in a vessel lined with lead and provided with a pipe for carrying away the vapours, in such manner that both liquids run in at the same time, and that a nearly neutral, but faintly acid, liquid is formed. It is well in preparing the concentrated ammoniacal liquor to remove the carbon dioxide as much as possible in order to get rid of the troublesome effervescence in the process of saturation. Towards the end of the operation the temperature rises considerably, and there is much more danger of ammonia being carried away by the vapours, which must, of course, be dealt with in the ordinary manner to destroy the hydrogen sulphide (*cf.* pp. 1496 *et seq.*). When the vessel is full, the supply is stopped, and the liquor is concentrated by a steam-coil up to the crystallizing point. The crystallization takes place in vessels lined with lead and the crystals turn out quite white, if made from sewage. As very large crystals are not liked in trade, the contents of the crystallizers are stirred up two or three times a day. Naturally the size of the crystals also depends to a great extent on the concentration of the solution. Where a solution of ammonium chloride is boiled down in iron vessels, as is sometimes done (especially in England) in order to allow of direct firing and to economize fuel, the liquid must always be kept alkaline, and the loss of ammonia occurring during the evaporation by the dissociation of a little ammonium chloride must always be made up. If the liquid once becomes acid, it quickly dissolves iron in the form of ferro-ammonium chloride, which is not decomposed by an excess of ammonia. Evaporation in lead is dearer, but much safer if any contamination with iron is to be avoided. Even metal taps must be dispensed with, and must be replaced by indiarubber tubing and pinchcocks.

R. W. Hilgenstock (*Amer. Gas Light J.*, 1906, pp. 849 *et seq.*) treats weak liquor in the usual manner, first by steam, then by lime, and absorbs the gases in water to yield a strong, pure solution of ammonia. This is run into neutralizing tanks, made of wood with a lining of hard-burned clinkers, joined by a mortar made of sulphur and glass-dust, with two inlet pipes (for concentrated ammoniacal liquor and hydrochloric acid) reaching nearly down to the bottom, made of hard rubber, and a paddle for mixing the liquids. A wooden stack with a steam jet draws off the noxious vapours into the chimney stack or into a sulphur recovery apparatus. The inlet valves are regulated in such manner that the solution is always acid; but when the tank is almost full, the acid valve is closed and more ammonia liquor is run in until a sample, tested with methyl-orange, shows a clear "wine-yellow" colour. The liquor is now drawn off by means of a rubber hose into a wooden tank, where it is mixed with the mother-liquor from the crystallizing tanks, being always kept slightly alkaline, to avoid action on the pumps and coils in the concentrating vats. These are made of wood, lined with hard-burned clinkers laid in best Portland cement, with a leaden or cast-iron steam-coil, with a cover and elbow pipe, leading to a coke scrubber for removing the smelling gases, of which the pyridine is especially troublesome. The evaporation is continued until the solution is saturated at 100°, which is recognized by a white skin forming on the top. The liquor, after remaining at rest for a little while, in order to deposit impurities, is run into the filter-tanks, made of pitch-pine, with a false bottom, on which boneblack of different sizes is packed, with a filter cloth on the top, and a small steam-coil to prevent crystallization within the filter itself. The filtered liquor is run into wooden crystallizing tanks, fitted with wooden sticks to which the crystals adhere; the crystallization is complete in five or six days. The crystals are drained in a centrifugal extractor (the drum of which is made of copper) and afterwards (with continuous turning over) on a drying table, consisting of glazed terra-cotta tiles on small brick piers, heated by exhaust steam from the coils in the concentrating-pans.

The sheds, where the evaporation and crystallization is carried on, should not be built of iron, upon which the vapours of ammonium chloride have a destructive action, but of wood or concrete. The store tank for the concentrated ammoniacal liquor should be protected by a tar paint; wherever possible, it should be placed outside the shed. The store tanks for hydrochloric acid can be made of wooden tubs, lined with gutta percha, or, preferably, of stoneware. Wooden tubs provided with an acid-proof asphalt lining are also employed, but in many cases have failed to answer their purpose.

The manufacture of ammonium chloride from ammoniacal liquor can also be carried out in a similar way as that of ammonium sulphate, *i.e.*, allowing the aqueous vapour to distil off during the saturation. This is done, *e.g.* by Carl Francke, at Bremen, in the following way:—The gas coming out of the ammonia still, which contains a great deal of steam, is partly dehydrated in a reflux-cooler and is then passed into a stoneware saturator, charged with hydrochloric acid of sp. gr. 1·1. The gas enters below the surface of the acid where the NH_3 is retained, whilst H_2S and CO_2 go away; the exit gases are treated exactly as described in the case of ammonium sulphate, *supra*, pp. 1496 *et seq.* When the liquid in the saturator has been nearly saturated, it consists of a solution of about 25 per cent. NH_4Cl, which is concentrated in pans, made of wood lined with lead and heated by lead steam-coils lying at the bottom. When a skin of sal-ammoniac is forming at the surface, the concentrated liquor is run into another pan, made of brick-work lined with lead, where it is evaporated up to crystallization by means of fire gases or steam. The solid ammonium chloride, forming here, is thrown by means of wooden scoops on to an inclined draining stage, placed at such an elevation that the mother-liquor can run back into the pan, and is further dried by centrifugalling. The sal-ammoniac obtained in this way, or by any other direct process, is certainly never a pure product.

Beimann (B. P. 9358, 1911) produces ammonium chloride from the crude gas by fractional saturation. The first condensate is always richer in ammonium chloride than those following it, and is put back into the still or the coke-scrubber.

Barnick (*Chemische Apparatur*, 1915, p. 33) describes the manufacture of ammonium chloride from ammoniacal liquor, without adducing any new matter.

Strommenger (*Z. angew. Chem.*, 1914, i., p. 518) makes a similar description. His apparatus is supplied by the Berlin-Anhaltische-Maschinenbau Aktien-Gesellschaft, Köln-Bayenthal, which has taken out Ger. Ps. 271421 and appl. St.18522 for the preparation of ammonium chloride. So has Hinselmann, Ger. P. appl. H63772.

Manufacture of Ammonium Chloride from the Sulphate.—For this purpose a concentrated solution of the latter is mixed with an equivalent quantity of common salt, and the whole is well agitated and boiled down, during which process monohydrated sodium sulphate is precipitated and ammonium chloride remains in solution:

$$(NH_4)_2SO_4 + 2NaCl \rightleftharpoons Na_2SO_4 + 2NH_4Cl.$$

The sodium sulphate is fished out with perforated spades and drained on copper plates, the liquor always running back into the pan. The salt is washed with a little water. The evaporation is continued until no more coarse crystals fall down, and the liquid begins to be covered with an opalescent pellicle of salt, which shows that the sodium sulphate is nearly all removed. The liquid is now allowed to cool in leaden vessels; and the crystallizing ammonium chloride is first washed with a solution of the pure salt, then with pure water.

Naumann (B. P. 654, of 1908; Fr. P. 378445, of 1907; Ger. P. 196260), instead of employing molecular proportions of ammonium sulphate and sodium chloride, uses an excess of the latter; in this case, on cooling, the ammonium chloride crystallizes out free from sulphate. The hot final solution should contain less than 75 parts of NH_4Cl to every 100 parts of water. Example: Dissolve 80 parts ammonium sulphate in 100 water at 70° C. or above, add 15 sodium chloride with agitation, digest for an hour or two, decant the liquor from any residue, and set to cool, when NH_4Cl, free from sulphate, will be separated. To the mother-liquor add ammonium sulphate and repeat the process with further addition of sodium chloride.

Freeth and Cocksedge (B. P. 26263, of 1909; Fr. P. 414682; U.S. P. 970909) mix equivalent quantities of ammonium sulphate and sodium chloride at about 103° with just enough water to obtain a saturated solution of ammonium chloride and sodium sulphate; the NaCl is completely decomposed, and on cooling down to 30°, ammonium chloride crystallizes out, free from sodium sulphate, if before the refrigeration a little water or solution of ammonium chloride (less than 4 per cent. of the total volume) has been added. For that purpose ordinary brine may be employed. According to the B. P. 86, of 1910 (Ger. P. 226108; U.S. P. 1035696) of the same inventors pure ammonium chloride is obtained by agitating, at about 103°, 97 parts ammonium sulphate, 86 sodium chloride, and 106 water for about an hour, and filtering at the same temperature; the mother-liquor, after adding 6 parts of water or ammonium-chloride solution, is cooled down to 30°, to separate the ammonium chloride.

Nouvelle (Fr. P. 408814) neutralizes sodium bisulphate with ammonia, allows any normal sodium sulphate formed to crystallize out, and treats the solution with sodium chloride. From the ammonium chloride thus formed the sodium sulphate is separated by fractional crystallization.

Th. Schmidtborn (U.S. P. 330155) decomposes ammonium sulphate and *potassium chloride* into potassium sulphate and ammonium chloride. He describes his process as follows:[1]—In a lead-lined tub, with false bottom and agitating-gear, 2½ tons ammonium sulphate are dissolved in water or in the washings of potassium sulphate up to sp. gr.=71° Tw. The liquor is heated to boiling, and the exactly equivalent quantity of potassium chloride is put in, with constant agitation. The boiling is continued for another ten minutes; the liquor is allowed to settle for half an hour, and is then run off. The potassium sulphate for the most part remains behind on the false bottom, and can be freed from ammonium salts down to ½ per cent. by washing. Thus 70 per cent. of the total potassium sulphate are recovered. The washings are used for making a fresh solution of ammonium sulphate. The hot liquor on cooling deposits more potassium sulphate, and a further quantity on concentration. By a second concentration and cooling down, a mixture of salts is obtained in two distinct layers: the upper three-fifths consisting of 94 per cent. ammonium chloride, with 6 per cent. potassium and sodium sulphate and sodium chloride; the lower two-fifths consisting of 78 per cent. ammonium chloride and 22 per cent. potassium sulphate. The upper layer can be converted into 98 or 99 per cent. ammonium chloride by mere washing; the lower by recrystallizing. For the latter object, the salt is suspended in perforated trays in boiling liquor, which dissolves out the ammonium chloride within a few minutes; the crystalline potassium sulphate remains behind on the trays and is lifted out in them. On cooling, the ammonium chloride crystallizes out, and is drained by means of a centrifugal machine, as well as the potassium sulphate. The former is also stove-dried; the latter is sold as it is. This process, which has been actually carried out by the inventor, is claimed by him, as an improvement upon the analogous process with sodium chloride, because there is no partial decomposition on the liquors cooling down. He also claims that the value of the potassium chloride is more than covered by that of the sulphate obtained.

Other Processes for the Manufacture of Ammonium Chloride.

Kuentz has proposed to make sal-ammoniac by direct distillation of ammoniacal liquor into an acid solution of phosphate of lime, produced by dissolving native phosphate of lime in hydrochloric acid :

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[1] *Chem. Zeit.*, 1886, p. 1499.

$$Ca_3(PO_4)_2 + 4HCl = CaH_4(PO_4)_2 + 2CaCl_2.$$

The reaction taking place with the ammonium carbonate distilled into the solution, or added in the shape of concentrated liquor, produces a precipitate of dicalcium phosphate and calcium carbonate, which is a much more valuable manure than the native phosphate, and a solution of ammonium chloride. The object of this process is to save the acid required for making superphosphate or "precipitated phosphate," as this acid is altogether turned into sal-ammoniac; but the process does not seem to have found practical application. Its theoretical equation would be :—

$$\begin{aligned} &CaH_4(PO_4)_2 + 2CaCl_2 + 2(NH_4)_2CO_3 \\ &= 2CaHPO_4 + CaCO_3 + 4NH_4Cl + CO_2 + H_2O. \end{aligned}$$

Another process proposed by Kuentz consists in treating the gas-liquor with impure ferrous chloride, made from pyritous schist and common salt. There is thus obtained a solution of ammonium chloride and a precipitate of ferrous carbonate and oxide mixed with a little sulphide, which is an excellent material for purifying coal-gas. In this process no noxious gases are given off.

Another process is one in which "concentrated gas-liquor" (p. 1344) is mixed with a solution of calcium chloride (which is a waste-product of many chemical operations and without any value) till all the lime is precipitated; the mass, passed through a filter-press, yields cakes of calcium carbonate and a solution of ammonium chloride, which should be acidified with hydrochloric acid, in order to destroy any sulphide. The calcium carbonate carries down most of the impurities; so that even ammoniacal liquors from the destructive distillation of bones and other animal matters can be treated in this way for pure ammonium chloride.

Gentles (B. P. 2224, of 1878) distils the ammonium carbonate, etc., from gas-liquor into a crude solution of calcium chloride, contained in a vessel with agitating-gear. The solution is separated from the precipitate, is acidified in order to precipitate any arsenic as trisulphide, and the clean filtrate is again made alkaline with ammonia, to precipitate any iron as oxide. These processes, founded on the application of calcium chloride, appear to deserve attention.

Dubosc and Henzey (*J. Soc. Chem. Ind.*, 1890, p. 614) decompose gas-liquor by the exact proportion of a solution of calcium and ferric chloride, with formation of FeS and $CaCO_3$. The mixed liquids are allowed to stand for twelve hours, when the upper two-thirds can be drawn off clear. The precipitate is an excellent gas-purifier. The solution, testing about 7° Bé., is evaporated in small iron pans to 13° Bé.; the vapours pass into a chimney. The concentrated liquor is run into wooden coolers, where it remains a fortnight. During this time the upper crust of crystals is broken up every day, to obtain needle-shaped crystals. Cubical crystals are obtained by adding to the liquor 5 per cent. of a solution of ferric chloride (*cf.* Adler, *infra*). The crystals are drained and dried at 50° or 60°, or carefully roasted in a reverberatory furnace. A brownish-yellow colour of the salt (which seems to be preferred in France) is obtained by adding a little slaked lime (which evidently produces ferric hydrate from adhering ferric chloride). A "refined" product is obtained by stopping the concentration at 11° Bé., precipitating the iron by ammonium sulphide and boiling down the clear liquor in enamelled cast-iron pans. Any cracks in the enamel should be mended by a mixture of cement, silicate of soda, and hydrofluosilicic acid. The concentrated liquor is allowed to crystallize in earthenware dishes.

The same authors describe the manufacture of ammonium chloride from ammonium sulphate by double decomposition with calcium chloride, or, preferably, ferrous chloride (obtained on pickling iron), allowing the ferrous sulphate to crystallize out, removing the iron from the mother-liquor as above, and obtaining the ammonium chloride from the last liquor.

A detailed description of the manufacture of ammonium chloride from *waste-liquors of ammonia-soda works* is given by Adler.[1] After driving off the ammonia (both "volatile" and "fixed") in the ordinary steam-column, the residual liquor is clarified by subsidence, and the clear liquor freed from lime by treatment with carbonic acid. After filtration, the liquor is concentrated in an ordinary salt-pan to exactly 20° Bé., up to which point no sodium chloride falls out. The concentration is continued in a smaller pan, fishing out the sodium chloride at regular intervals. At 32° Bé. most salt is removed, but an almost quantitative removal requires concentration to 40° Bé. in winter, or 44° Bé. in summer. The cooled and clarified liquor then contains only about 3 per cent. NaCl; 1 litre of winter liquor contains about 680 g., of summer liquor 580 to 600 g. calcium chloride.—The second liquor required, viz., a solution of ammonium carbonate, is obtained by washing the gas given off on calcining the sodium bicarbonate; it contains at least 2 per cent. of ammonium carbonate, with a little free NH_3, etc.

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[1] *Z. angew. Chem.*, 1899, pp. 201 and 226.

These liquors are now mixed in the cold, after having diluted the $CaCl_2$ solution to 10° or 20° Bé., in order to obtain the $CaCO_3$ in the proper shape, leaving a small excess (3 to 5 per cent.) of $CaCl_2$. The vessel in which this is effected is cylindrical, with a conical bottom, provided with stirring-gear and an outlet-cock at the bottom. The calcium carbonate should be quickly and completely removed when formed, to prevent the conversion of the rhombic arragonite crystals into rhombohedric calcite crystals. The decomposition is finished when a filtered sample yields no precipitate with calcium chloride. If free NH_3 is present, the solution formed must be treated with the exactly corresponding quantity of hydrochloric acid. The separation of the precipitated calcium carbonate from the ammonium-chloride solution is best effected by a wooden filter-press, to prevent contamination with iron. After pressing, the residue is first washed with washings from a previous operation, then with pure water, and then treated with a current of air; the cakes of calcium carbonate leave the press with 50 per cent. moisture, and can be dried in various ways.

The boiling-down of the ammonium-chloride solution is best performed in lead-lined pans; the small quantity of lead passing into the product is immaterial for technical purposes. The heating is done by means of leaden steam-coils, up to the time when a pellicle of salt appears on the surface. The liquor is now run off into lead-lined iron or wooden coolers, which may be shallow or deep. For some purposes small crystals are preferred, in which case the liquor is stirred from time to time. The mother-liquor remaining after crystallization is evaporated separately and is eventually removed, when too impure.

The crystals formed in the first liquor are at once marketable, after draining and drying, which is best done on wooden frames covered with jute sacking, in steam-heated stoves. The crystals formed in mother-liquors must be freed from adhering calcium chloride by recrystallization.

Specially fine crystals, according to Adler, can be obtained as follows:—Mother-liquor, containing more $CaCl_2$ than the first liquor, is boiled down up to the formation of a salt pellicle, then mixed with an equal volume of first liquor and at once run into the coolers, during which time it is mixed with a similar solution of cupric sulphate (0·01 g. to 1 litre). After twenty-four hours the first octohedric crystals are formed at the sides and the bottom of the vessels, which increase and are of remarkable transparency and hardness, not obtainable without the cupric sulphate. Sometimes crystals 4 inches in length are thus obtained; usually they are 2 inches or a little more.

The Solvay Processes Company (U.S. P. 805581) obtain ammonium chloride by the simultaneous action of dry NH_3 and CO_2 on a concentrated (1·38 sp. gr.) hot solution of calcium chloride. The $CaCO_3$ is removed by settling out, and the solution on cooling yields the ammonium chloride.

A very peculiar process is that of Th. Heskin (B. P. 2491, of 1884). He decomposes sodium borate by sulphuretted hydrogen, dissolves the separated boric acid in strong liquor ammoniæ, and decomposes the ammonium borate with common salt, whereby sodium borate is regenerated.

Duvieusart (B. P. 20613, of 1907) makes ammonium chloride by adding sea-salt to a saturated solution of ammonium sulphite at 40° C., and raising the temperature to 95°. Sodium sulphite is deposited and separated hot from the mother solution, which, on cooling to 40°, deposits ammonium chloride. The mother solution now remaining is again charged with sulphite of ammonium and sea-salt, heated to 95°, and treated as before.

Dr Friedrich & Co. and F. Hirsch (B. P. 11123, 1909; Ger. P. 228538) pass into a solution or suspension of sodium chloride in water sulphur dioxide and ammonia, whereby the reaction:

$$2NaCl + 2NH_3 + SO_2 + H_2O = Na_2SO_3 + 2NH_4Cl$$

is produced. Into a mixture of 180 parts water and 120 parts common salt pass at first a little SO_2, afterwards about equivalent quantities of SO_2 and NH_3, keeping the liquid slightly acid up to the end of the operation; lastly, they make the liquid neutral, whereupon the percentage of SO_2 in the solution is about 9 or 10 parts in 100 vols. The sodium sulphite, crystallized out while the liquor is hot, is removed, and the liquor is allowed to cool down to 40°-35°, in order to allow the ammonium chloride to crystallize. The mother-liquor remaining from this is worked up as follows: 370 parts of this mother-liquor, of sp. gr. 1·231 at 30°, containing 36·9 parts Na_2SO_3, 87·7 NH_4Cl, 4Na_2SO_4, and about 240 water, are mixed with 60 parts sodium chloride, and into this suspension 20 NH_3 and 36 SO_2 are passed. The liquid is strongly heated up to 112°; anhydrous sodium sulphite is separated in the solid state and removed from the liquid while hot. The remaining liquid is allowed to cool down to about 35°; the sal-ammoniac crystallized out is removed, the necessary quantity of common salt is again put in, and again SO_2 and NH_3 are passed in at the same time until the conversion is complete. The B. P. of Friedrich No. 6684, 1911 (Fr. P. 402872) extends this process to include the manufacture of sulphites of barium, strontium, calcium, magnesium, and zinc.

French (U.S. P. 882460) drenches carbonized coal with strong brine and burns it in a current of air containing at least 10 per cent. steam, whereby ammonium chloride is said to be produced.

Ammonium chloride occurs sometimes in somewhat considerable quantities among the constituents of *coal-tar*. R. Otto & Co. (Ger. P. appl. O7042) obtain pure ammonium chloride as a by-product in the manufacture of ammonium sulphate from the gases of coal-distillation by allowing the mother-liquor, when the percentage of ammonium chloride in it has increased to 13-15 per cent., to cool down to 50°-70°, whereupon the chloride crystallizes out almost chemically pure *before the sulphate*. If in a preliminary test sulphate has crystallized along with the chloride, the liquor is slightly diluted. The ammonium chloride obtained in this way is free from tarry substances, and requires no re-crystallization before being sent out into the trade.

Ammonium chloride is used to a considerable extent in the process of *galvanizing iron, i.e.*, coating it with zinc, and accumulates in the scoria formed in this process, from which it can be obtained by lixiviation. Another by-product formed in this process is the solution of *ferrous chloride*, formed in purifying the iron before the galvanization by means of hydrochloric acid. Wülfing (Ger. P. 921744) utilizes this solution for the manufacture of ammonium chloride, by partially saturating it with aqueous or gaseous ammonia, boiling it with injection of air, and completing the saturation with NH_3, whereupon a precipitate of black magnetic ferroso-ferric oxide is formed, which is an article of trade, and sal-ammoniac is obtained by boiling down the mother-liquor.

The Berlin-Anhaltische Maschinenbau A. G. (Ger. P. 271421) obtains ammonium chloride from the gases evolved in the destructive distillation of coal, wood, peat, etc., by treating the water condensed from the gases with hydrochloric acid and alkaline or earth-alkaline chlorides, whereby the NH_4Cl already existing in that water is recovered as well.

Ammonia, contained in gases, vapours, or liquids, is obtained by the A. G. Chem. Fabr. Pommerensdorf (Ger. P. 281095) in the form of a highly concentrated ammonium salt solution by means of an acid gas, especially SO_2 or HCl.

Properties of Crude Ammonium Chloride.

The *crude ammonium chloride* is coloured more or less dark by tarry matters, and contains other impurities, especially ammonium sulphate and thiosulphate, as well as moisture. It is dried in layers 4 inches thick, on metal plates heated by the waste heat of the subliming-pans, but not to the point of volatilization. Here the water and free acid are volatilized, and the tarry matters are mostly carbonized. The roasted salt is of a grey-white colour, and should be conveyed as quickly as possible into the subliming-pots, lest it should again attract moisture. If the crude salt has been made by direct saturation of gas-liquor with hydrochloric acid (a process which ought to be given up as quite irrational, and as causing a great nuisance; *cf.* pp. 1329 and 1527), in drying or roasting it produces a very bad smell, which is absent when the salt has been made from distilled ammonia.

Gebr. Hinselmann (Ger. P. 284641) purify crude sal-ammoniac, as it is obtained when coking coal, from the coloured tarry substances by heating to 200°-250° and recrystallizing.

Purification of Ammonium Chloride by Sublimation.

Sometimes the subliming is done in long rows of earthenware pots or glass carboys. This is the process used in Egypt and other Oriental countries, and it is still practised in France, since the buyers there demand the small cakes obtained by this process. But this is expensive, on account of the labour and the loss of the vessel in each operation. Hence in England iron pots are exclusively used, either cast in one piece or composed of several pieces, 3 to 9 feet in diameter. Large pots are far preferable to small ones, as the latter require nearly as much fuel, labour, and time for working off as the former. They are lined with firebricks, and are heated by a fire from below and by annular flues all round. Their bottoms are, by preference, concave, so as to present a larger heating-surface. The pots are covered with concave plates, provided in three places with rings for chains, by means of which they can be lifted off by a travelling crane, etc. The covers are perforated in the centre; the aperture is closed by an iron rod, which is removed from time to time, in order to allow the permanent gases to escape. They are covered with some non-conductor of heat. Pots 3 ft. wide hold 10 cwt., those 5 ft. wide 15 to 18 cwt., and those 9 ft. wide 2 to 2½ tons of salt.

The operation must be exactly regulated. At first a brisk fire is made, but this is slackened directly the sublimation commences, since at a very high temperature too much empyreumatic matter is evolved and disturbs the solidification of the salt. At too low a temperature the sublimate is loose and not transparent, which makes it difficult to sell. The cover ought to be at such a heat that a drop of water begins to boil on it and evaporates quickly. The first layer adhering to the cover is always brownish, probably because a little water always remains in the roasted salt, which condenses on the cover and loosens ferric oxide. Later on a coloration may be caused by ferric chloride. The sublimation may last from 5 to 9 days, but is usually interrupted after a week by lifting the cover, the fire having been damped up some time before. The sublimation is not driven to the last; for then the temperature would rise too high, the carbonaceous impurities would be decomposed, and the vapours would injure the appearance of the sal-ammoniac. On the cover is found a layer from 2½ to 4 inches thick, which is knocked off. The above-mentioned brown stratum is hacked off with a hatchet or planed off.

The French subliming-process is illustrated by Figs. 333 and 334. It is carried on in *earthenware pots*, P, about 18 inches high and 12 to 14 inches wide, of which about 20 are placed, in two rows, in a galley-furnace heated at one end. The pots stand on an arch, perforated by pigeon-holes, *o o*; they are supported at two-thirds of their height by the cast-iron plate F, on which a layer of sand is spread quite up to the top of the pots. After being charged with dry crystallized ammonium chloride, which is sometimes mixed with about 20 or 30 per cent. of animal charcoal, they are placed in the furnace, covered up with sand, and at first heated gently, in order to avoid cracking. The moisture still present escapes through the openings *s s*, and soon the thick white vapours of sal-ammoniac appear, whereupon an ordinary flower-pot, *p*, is put on as a cover. The sublimate collects partly in the upper portion of the pots P, and partly in the flower-pots, *p*. The openings *s s* gradually get stopped up; and towards the end of the operation, when the fire has to be increased so as to produce the dense and translucent appearance of the product required in commerce, there is a certain pressure in the apparatus. In order to obtain sufficiently large cakes, the pots must be charged several times over again. For this purpose the openings are cleared again and the operation is repeated. After two or three charges the cakes are large enough; the pots are now taken out when sufficiently cool, and are broken in order to get out the sublimate. The whole takes about two days.

In some places, in lieu of earthenware pots, *glass flasks* or *carboys* are used on account of cheapness. These are usually about 1 foot wide and 2 ft. high, and hold 20 lb. of the mixture of dry ammonium chloride and charcoal. They are placed in a double row of eight or ten each in metal pots, heated by a

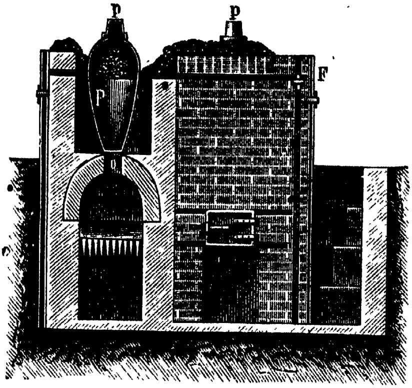


FIG. 333.

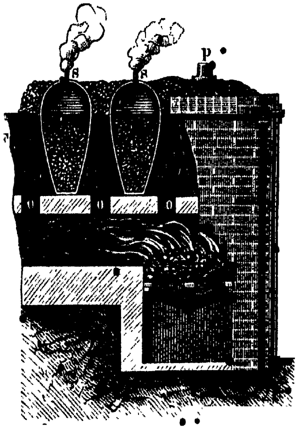


FIG. 334.

galley-furnace. The pots serve as sand-baths, and the flasks are placed about two-thirds in the pot; the last third projects outside, but is covered with a layer of sand up to the neck, which is covered with a piece of sheet-lead. When this appears covered with a glassy sublimate of sal-ammoniac, the projecting part of the flask is cleared of sand, and care is taken to prevent the lead from adhering too fast to the flask, by knocking on its lower side from time to time. When the sublimate is glass-like, and the lead plate, on knocking from below, is no longer lifted up by the vapours evolved, it is left lying on the top; but the upper opening must never be allowed to become entirely stopped up, which is prevented by boring in with a pointed iron. The operation lasts from twelve to sixteen hours. The lead covers are then taken away, and are replaced by corks or by pieces of cotton-wool, and the whole is allowed to cool down slowly. During the cooling the sal-ammoniac expands and cracks the glass. The cake, freed from glass, is scraped with a knife, to remove all dirt, and is packed in the shape of loaves; it is crystalline and perfectly white.

The French sal-ammoniac being thus made in earthenware or glass vessels, is purer than the English article sublimed in iron pots. The destruction of the subliming-vessels at each operation makes it a costly product; but it might no doubt be made much more cheaply in stoneware vessels consisting of two parts, which would stand a number of operations.

Some French consumers require the sublimed sal-ammoniac to look as grey and dirty as that formerly made in Egypt from camels' dung; this is effected by adding some greasy matter to the salt before sublimation, or in small portions during the operation, so that some soot gets mixed with the sal-ammoniac. Otherwise it ought to be white, transparent, of fibrous texture, and firm, not porous and light. Sometimes a few per cent. of monocalcium phosphate or of ammonium phosphate are mixed with the salt before subliming, in order to retain any iron. This is also recommended by Adler (*loc. cit.*), who adds to the crude ammonium chloride 20 or 25 per cent. commercial superphosphate, and heats without putting on the lid, until white vapours begin to appear. The operation proceeds all the better the slower the heating is performed. The lid should be milk-warm only.

Calvert proposed, in order to make the sublimation cheaper and continuous, and to obtain the product in a shape more convenient for use, to dry the muriate of ammonia very briskly and distil it from a set of fireclay retorts, alternately charged into large brick chambers covered with a smooth coating of cement inside, on which the sal-ammoniac would be deposited as a fine powder. This process, which looks very rational indeed, was tried on the large scale, but was given up, and is not in use anywhere at present, probably because the consumers insist upon the fibrous transparent texture of the product, which they believe (although erroneously) to guarantee its purity. Calvert also tried adding animal charcoal and phosphates before subliming; but his sal-ammoniac was never free from iron.

Commercial sal-ammoniac appears in the form of cakes or disks, weighing from 10 to 40 lb., sometimes as much as 1 cwt., white, translucent, of fat-like brilliancy, hard and resonant. They are formed of parallel layers of a fibrous texture.

Pure Crystallized Salt (*Muriate of Ammonia*).

Besides sublimed sal-ammoniac, the crystallized salt, usually called *muriate of ammonia*, is also found in the trade at a much lower price. To obtain this, the crude salt is once or several times recrystallized, and the solution each time filtered through animal charcoal. It is also made into the shape of loaves, the crystals being stirred up to a paste with a hot saturated solution, and the whole being allowed to solidify in conical sugar-moulds of glazed earthenware. The opening at the bottom is at first closed by a plug, which is removed after a few days; the mother-liquor then drains off. The loaves are taken out by inverting the moulds, and are dried in a stove; they turn nearly as hard as loaf-sugar. Most ammonium chloride, however, is sold in the form of sublimed sal-ammoniac. The consumers insist upon getting it in this shape, although it generally costs twice as much as the crystallized salt, and is no better. An attempt made by the French Company Lesage to replace it by strongly compressed cakes of crystallized salts, in disks of 4 ins. diameter and 1 in. thick, failed for want of support from the buyers. Hempel (*Berl. Ber.*, xxi., p. 897) mentions that this was done by strong hydraulic pressure at temperatures between 50° and 100° C.

A description of the manufacture of crystallized ammonium chloride, containing nothing new, is made by Barrik in *Chem. Apparatur*, 1915, pp. 33-34.

Purification of Ammonium Chloride from Iron.

For some purposes that salt should be entirely free from iron. Formerly it was believed that this was always the case with colourless sal-ammoniac; but Wurtz has shown that only ferric chloride is indicated in sal-ammoniac by the ordinary reagents, while ferrous chloride cannot be discovered either by the colour or by the ordinary reagents. The ferrous can be formed from the ferric chloride by the reducing action of sal-ammoniac itself, thus:—

$$3Fe_2Cl_6 + 2NH_4Cl = 6FeCl_2 + 8HCl + 2N.$$

In order to make a product entirely free from iron, a little chlorine gas is passed through the boiling-hot solution of ammonium chloride (an excess of chlorine would produce that fearfully explosive substance, nitrogen chloride); ammonia is added, which precipitates all the iron now present as peroxide; and liquid is quickly filtered and crystallized. A salt free from iron is said to be obtained also by adding a little calcium phosphate before sublimation (see p. 1542).

The preparation of chemically pure ammonium chloride for the purpose of atomic-weight determinations is described by Hinrichsen in *Z. anorg. Chem.*, 1908, lviii., p. 59, and *Z. angew. Chem.*, 1908, p. 1081.

Uses of Ammonium Chloride.

Ammonium chloride is used in pharmacy, in soldering, in galvanizing iron; for making the ordinary rust cement from 100 parts iron filings, 4 brimstone, and 1 sal-ammoniac; in calico printing; in the manufacture of colours (for the last-named purpose it is mostly required to be free from iron; *vide supra*).

A not inconsiderable quantity of crystallized ammonium chloride is used for feeding the Leclanché cells generally employed in telegraph-offices, etc. For this purpose it should be free from lead, which is very injurious to the working of the cells, and it should therefore be freed from metals by ammonium sulphide.

Whitehouse (B. P. 15140, of 1907) prepares ammonia and chlorine or hydrochloric acid from ammonium chloride, by heating it to 300° C. in mixture with the oxides or oxychlorides of cerium, thorium, didymium, lanthanum, or yttrium. NH_3 and water are expelled. The resulting chlorides of the above metals are heated in a current of air or steam, whereby Cl or HCl are evolved, and the oxides of the metals remain behind.

Seeber (Ger. P. 113895) uses ammonium chloride for preparing a special kind of soap ("Salmiakseife").

Naef (Ger. P. 115249) produces ammonia and magnesium chloride by heating a dry mixture of ammonium chloride and magnesia in an inclined revolving cylinder, from which the liquefied magnesium chloride is constantly run off on one side, fresh mixture being constantly introduced at the other end; a current of a heated inert gas traverses the cylinder, whereby this is sufficiently heated and the ammonia is carried away before it can be decomposed.

Statistics.

There are no statistics on the production of ammonium chloride in the various countries.

Enormous quantities of ammonium chloride are produced as an intermediate product in the manufacture of ammonia-soda; but these are always reconverted into free ammonia, to be used over again, and we must refer to the treatment of this subject in Lunge's *Sulphuric Acid and Alkali*, vol. iii.

	The German Empire imported	And exported ammonium chloride:
In 1907	396 tons	2968 tons
,, 1908	271 ,,	2473 ,,
,, 1909	251 ,,	3105 ,,
,, 1910	206 ,,	3601 ,,

AMMONIUM BROMIDE, NH_4Br.

Isleib (Ger. P. 286183) obtains this salt by moistening coal with liquor containing bromine, heating, mixing the sublimate produced with the condensed aqueous liquor, concentrating this by heating at 60°, separating the ammonium chloride crystallizing out, evaporating the residual solution of ammonium bromide at 40°, until a saline crust forms, then mixing the liquid with fifteen times its volume of 95 per cent. alcohol, and after twenty-four hours separating the alcoholic solution of ammonium bromide.

AMMONIUM FLUORIDE, NH_4F.

This salt forms hexagonal scales or prisms, of sharp, salty taste, deliquescent in moist air; its properties are described *supra*, p. 1314. It is obtained by passing hydrogen fluoride into liquor ammoniæ. In the moist state it decomposes silicates at ordinary temperatures, in the dry state at higher temperatures, and is therefore employed for etching glass. On evaporating its solution at 40° an acid salt, NH_4F,HF, is formed which crystallizes in colourless prisms, but is a little deliquescent. It must be kept in bottles of lead or guttapercha.

For manufacturing it on the large scale, T. W. Mills (Ger. P. 94849) mixes finely ground ammonium sulphate with ground fluorspar, and heats the mixture gradually above 350° C. in a cast-iron pan, lined with a thin layer of gypsum, and provided with a concave lead lid, cooled on the outside by water. The ammonium fluoride formed by the reaction

$$(NH_4)_2SO_4 + CaF_2 = CaSO_4 + 2NH_4F$$

sublimes with a little sulphate, and is condensed on the inside of the lid.

This salt is employed for etching glass, for decomposing certain minerals containing rare earths serving for incandescent mantles, and for preparing certain fluorides (especially of antimony) employed in the dyeing industry.

The *testing* of the acid ammonium fluoride is performed by Brand (*Z. ges. Brauwesen*, 1904, p. 114) by titrating in the cold with fifth-normal baryta solution, employing litmus as indicator, expelling the NH_3 by boiling with a solution of NaOH, and absorbing it in fifth-normal sulphuric acid. Deussen (*Z. angew. Chem.*, 1910, p. 1257) found always too low values when titrating with baryta in the cold. He places the salt in a platinum crucible, adds an excess of standardized baryta solution, allows to stand over night under a glass jar, heating up first slowly, then gradually, to the boiling-point during four or five hours until there is no more smell of NH_3, washing everything into a beaker by means of standard hydrochloric acid, and re-titrating the excess of baryta, with phenolphthalein as indicator.

AMMONIUM FERROCYANIDE.

Description of its properties, *supra*, p. 1311.

Grossmann (B. P. 19988, 1907) obtains this salt by agitating gas-liquor with an excess of iron sulphide, in the presence of considerable quantities of ammonium sulphide, access of air being avoided. The necessary quantity of FeS is ascertained by a laboratory experiment. The clear liquor is distilled for NH_3 in the usual manner, and in the residual liquor the ferrocyanide is precipitated after acidification by adding iron compounds (*cf.* his B. P. 20387, of 1905, *supra*, p. 1450). He discusses this process in detail in *J. Soc. Chem. Ind.*, 1908, pp. 393 *et seq.* At that time apparently it had not yet come into use.

This salt has no direct technical application; if it is obtained in large quantities along with other cyanogen compounds, *e.g.*, in Bueb's gas-purifying process (Ger. P. 112459), in the liquid portion of the cyanide mud, it is transformed into sodium ferrocyanide by boiling with caustic-soda solution, with recovery of the ammonia.

AMMONIUM SULPHOCYANIDE (THIOCYANATE).

Description of its properties, *supra*, p. 1310.

This salt has come into use in dyeing and calico-printing, both directly and as a starting-point for the preparation of other sulphocyanides; hence it is manufactured on an industrial scale. It can be prepared by synthetical methods, but we first mention its recovery *from ammoniacal gas-liquor*. That liquor rarely contains more than 2·5 g. per litre, which does not pay working it directly for that salt, but this can be recovered from the residue remaining behind when the volatile ammonium compounds are expelled by steam. From this residue cuprous sulphocyanide can be obtained as a precipitate by adding a mixed solution of the sulphates of iron and copper. This was done by P. Spence (*Chem. News*, xviii., p. 119), who, after washing the precipitate, decomposed it by ammonium sulphide into copper sulphide and pure ammonium sulphocyanide. Similar to this, but hardly preferable, is the process of Storck and Strobel (*Dingl. polyt. J.*, ccxxxv., p. 156), who saturate gas-liquor with hydrochloric acid and precipitate the sulphocyanide by a mixture of cupric chloride and sodium bisulphite. The precipitate of cuprous sulphocyanide is washed, boiled with a solution of barium hydrate, and the barium sulphocyanide allowed to crystallize.

Parker and Robinson (B. P. 2383, 1890) add cupric sulphate to the waste liquor containing sulphocyanide, and pass SO_2 through it; the cuprous sulphate thus produced precipitates cuprous sulphocyanide.

Bower (Ger. P. 88052; B. P. 361, of 1896) transforms the cuprous sulphocyanide, prepared as above, into ferrous sulphocyanide and copper by addition of metallic iron.

Phipson (*Chem. News*, xviii., p. 131) mentions another process known in London, but does not say in what it consists.

The British Cyanides Co. and K. M. Chance (B. P. 6218, of 1908) wash coal-gas with a liquor containing alkaline polysulphide, which reacts with some of the cyanogen and forms thiocyanate and H_2S. The latter is passed, together with the gas, into a second washer, containing ammoniacal gas-liquor, in which free sulphur is kept in mechanical suspension; NH_3, H_2S, and S combine to form ammonium polysulphide, which removes the remainder of the cyanogen from the gas in the form of thiocyanate.

Crowther (B. P. 11964, of 1893) precipitates by CO_2 the lime from spent gas-liquor, and after settling treats the clear liquid with a paste of cuprous oxide, after which the mixture is slightly acidulated with HCl, and the cuprous sulphocyanide filtered off. By treating it with carbonates or hydroxides of alkalis the respective salts are obtained and the cuprous oxide is recovered.

We have seen before (p. 1206) that ammonium sulphocyanide occurs in large quantities in the ammonium salts made by lixiviating *spent oxide* from the purifiers of gas-works. It should be possible to separate the sulphate from the sulphocyanide by fractional crystallization. As a rule, 10 to 30 per cent. of the latter salt is present in the total ammonium salts (*cf.* Gasch, *Chem. Zeit.*, 1886, p. 2?4).

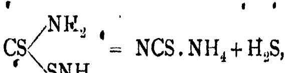
According to a patent of Marasse (Ger. P. 28137) the spent oxide, which after lixiviation still contains a great deal of sulphocyanide, is heated in a closed vessel, with an excess of lime and water, to a temperature exceeding 100° C. The products of this treatment are ferrous sulphate and calcium sulphocyanide, the latter of which is recovered by lixiviation, and serves for preparing other sulphocyanides.

Esop (*Chem. Ind.*, 1892, p. 6) discusses at length the treatment of spent oxide of iron. This contains the ammonium sulphocyanide irregularly dispersed in microscopical crystals. In cool places, protected from the weather, it keeps for some time, but at a somewhat higher temperature the sulphocyanide rapidly decomposes. This may take place on keeping the mass in deep layers in the damp state, which may even lead to the sulphur taking fire. The sulphocyanide in this case is converted into ferrocyanide and sulphate. In order to extract the sulphocyanide from the spent oxide, this must be finely ground and methodically lixiviated, preferably with the aid of filter-presses, by which liquors of sp. gr. 1·028 to 1·113 can be obtained. They are of yellow, green, or blue colour, but this vanishes later on during the further treatment. Weak liquors (sp. gr. 1·070 to 1·085) are not evaporated, but treated with cuprous oxide; those containing less than 2·3 g. sulphocyanide per litre are not worth treating at all. Stronger liquors are evaporated in vessels of nickel, lead, tin, aluminium, or preferably of enamelled iron. By evaporating to 22° or 27° Bé. and cooling, crystals of ammonium-sodium sulphate and ammonium sulphocyanide are obtained; from the mother-liquor by further evaporation a purer sulphocyanide is obtained, which on crystallization is of light yellow colour and contains 80 or 90 per cent. sulphocyanide. A purer article is made from this by precipitating both iron and sulphate by means of barium sulphide and recrystallizing. *Chemically pure* ammonium sulphocyanide is prepared by first converting it into the barium salt by means of caustic baryta, or by the action of barium sulphide on cuprous sulphocyanide. The former is done in closed vessels at 0·2 to 0·4 atmospheres' pressure, heated to 80° to 90° C., driving off the NH_3 by steam as quickly as possible. The second process causes no loss of sulphocyanide and saves any evaporation. The raw gas-liquor or extract from spent oxide is treated with cupric sulphate and sulphurous acid at ordinary temperatures, or at most at 40° or 50° C. The heavy light-grey precipitate of cuprous sulphocyanide, containing traces of sulphide, etc., is washed ten times by decantation and is decomposed by a solution of barium sulphide, of 15° Bé., in excess, which acts perfectly; whereas Crowther's proposal of employing alkaline hydrates or carbonates (p. 1548) yields a very imperfect result. It is preferable to employ at first an insufficient quantity of barium sulphide, and to decompose the remainder by an excess of this salt, reserving this liquor for the next operation. The colouring-matter is carried down with the copper sulphide. The clear solution of barium sulphocyanide is boiled down to 57° or 60° Bé., and yields very good crystals. The copper sulphide, after pressing and drying, can be roasted in pyrites-burners, and the remaining oxide used over again as before. The barium sulphocyanide, by treating with ammonium sulphate, yields perfectly pure ammonium sulphocyanide.

The *synthetical production of ammonium sulphocyanide* is performed by the action of ammonia and carbon disulphide at a temperature of 120° and 130° and at a pressure of 15 atmospheres.

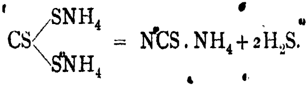
This process was carried out industrially for some time according to the patents of Tscherniak and Günzburg (Ger. Ps. 3199 and 16005). In the first instance ammonium thiocarbamate and thiocarbonate are formed, which, on heating, yield sulphocyanide and hydrogen sulphide:

(*a*)



$$CS\begin{cases}NH_2\\SNH_4\end{cases} = NCS.NH_4 + H_2S,$$

(*b*)



$$CS\begin{cases}SNH_4\\SNH_4\end{cases} = NCS.NH_4 + 2H_2S.$$

The process was carried out by passing NH_3 and CS_2 by means of an iron pump into a series of iron autoclaves, provided with agitating-gear, pressure-gauges, and thermometers, and with inlet and outlet taps, and heated to 120°-130° by means of a steam-jacket. The reaction takes place at a pressure of 15 atmospheres; when complete, the liquid is run into a still, in which at a temperature of 105°-110° the ammonium thiocarbamate formed is decomposed into ammonium sulphocyanide and H_2S. Any unchanged CS_2 also distils off. The plant used is minutely described in *Bull. Mulhouse*, 1882, p. 77. The factory was stopped after a short time, as there was no outlet for large quantities of ammonium sulphocyanide, and the working-expenses were too high.

Hood and Salamon (Ger. P. 72644) heat CS_2 and NH_3 with addition of an oxidizing agent, like MnO_2 or Fe_2O_3, with or without adding a base (CaO). The reaction is:

$$2CS_2 + 2NH_3 + MnO_2 + CaO = Ca(CNS) + MnS + S + 2H_2O.$$

The calcium sulphocyanide formed can be transformed into ammonium sulphocyanide by double decomposition with ammonium sulphate. The MnS is regenerated into MnO_2 by means of air in the well-known manner.

Modifications of this process, in which the addition of an oxidizing agent is avoided, are described by the British Cyanides Co., Ltd., in B.P. 14154, of 1894; Ger. Ps. 72644, 81116, 85492.

Goerlich and Wichmann (Ger. Ps. 87135 and 89811) produce ammonium sulphocyanide by heating 1 molecule of ammonium nitrite with 1 molecule CS_2 and 2 molecules H_2S to 150° in a pressure vessel; the reaction ensuing is:

$$NH_4NO_2 + CS_2 + 2H_2S = SCN.NH_4 + H_2O + S_3.$$

Goldberg and Siepermann (Ger. Ps. 83454 and 87813) add in the ordinary CS_2-process some sulphite or thiosulphate; the reactions are:

$$2CS_2 + 2NH_3 + NH_4.SO_3 = CSN.NH_4 + 3S + 3H_2O,$$
$$2CS_2 + 2NH_3 + NH_4.S_2O_3 = CSN.NH_4 + 4S + 3H_2O.$$

Applications of Ammonium Sulphocyanide.—That salt is employed in dyeing and tissue-printing. Formerly it was largely used or proposed to be used for the preparation of cyanides and ferrocyanides, especially owing to a prize offered by the Verein für Beförderung des Gewerbfleisses in Preussen, in 1877.

In the *analysis* of technical ammonium sulphocyanide, Pfeiffer (in Lunge and Berl's *Techn. chem. Unt. Meth.*, 6th ed., vol. iii., p. 373) prescribes liberating the NH_3 not by distillation with alkali, but by magnesia, because the former yield ammonia also with the nitrogen of the CNS group. For the same reason the azotometric method cannot be employed. The pure salt contains 22·38 per cent. NH_3.

The percentage of sulphocyanogen is found, according to Pfeiffer, by oxidizing with bromine and estimating the sulphuric acid formed by precipitation with barium chloride, the weight of which, multiplied by 0·2488, indicates the weight of the CNS present, of which pure ammonium sulphocyanide contains 76·30 per cent.

AMMONIUM CARBONATES.

The properties of commercial carbonate of ammonia (sal-volatile) have been described, *supra*, pp. 1315 *et seq.* We have seen there that it is a mixture or a compound of ammonium bicarbonate and carbamate, and as such is always formed on subliming. Hence the name frequently used for it, "ammonium sesquicarbonate," is incorrect, although the salt actually often has a composition approaching four molecules of NH_3 to three of CO_2.

In 1870 Divers (*cf.* p. 1315) found the article then manufactured to contain more ammonia, in the proportion of three molecules of NH_3 to two of CO_2; but in 1886 Hanekop and Reissmann, on the contrary, found an article consisting of one molecule of NH_3 to one of CO_2 (p. 1315), that is, really, ammonium bicarbonate; and Topf, in 1887, confirmed this with several samples of the commercial article analyzed by him (*Z. anal. Chem.*, xxvi., p. 158). Evidently different mixtures or compounds of ammonium salts have come into the trade at different times, and probably even at the same time, under the name of "ammonium carbonate."

Ammonium carbonate is *formed* in the destructive distillation of animal matters, and is often found as a solid deposit in the refrigerator, if the substances employed have been dry. This deposit, which forms brown crusts, was formerly known as "salts of hartshorn," and was always accompanied by a watery liquid, consisting of a saturated solution of ammonium carbonate, known as "spirits of hartshorn." Both are very much contaminated with tarry products, and cannot be purified by one redistillation, but only by a third distillation with boneblack. This manufacture is rarely carried out now.

Manufacture.—Commercial ammonium carbonate is now usually made by mixing ammonium sulphate with calcium carbonate and subliming. Calcium sulphate remains behind in the retort; and the mixture of ammonia, carbon dioxide, and aqueous vapour (which must always be present) condenses on cooling to solid carbonate of ammonia. A mixture of 1 part ammonium sulphate with 1½ or 2 parts of finely ground chalk, sometimes with a little charcoal powder, is heated in horizontal cylindrical cast-iron retorts, several of which are usually heated by the same fire, like gas-retorts. At first the heat should not be great; but at last it must attain redness.

The vapours are conveyed by a wide pipe into lead chambers, usually two or more in succession, provided with a door for the removal of the salt. From the last chamber the vapours pass through sulphuric acid, preferably trickling down in a small leaden coke-tower. In the chambers the condensation is effected entirely by air-cooling; but they may be surrounded by a jacket to cool them by water. Several operations are performed in succession, till a sufficiently thick crust has formed, which is loosened by blows outside with a hammer, and is completely broken off after opening the doors. This crust must not be allowed to become too thick, as otherwise the air-cooling will be too imperfect and the salt will become too hard and difficult to detach.

A convenient plan (Fig. 335) is to employ five retorts, *a a*, 18 in. in diameter and 7 ft. long, heated by one fire, *b*, with two condensing-chambers, B, C, both 8 or 10 ft. long and wide and 7 ft. high. The retorts may be charged alternately every eight hours. Each retort-cover has an aperture for a rake, to stir up the mass during the operation. The process in such an apparatus can go on for a fortnight before the chambers need be emptied, for which purpose the men adopt the precaution of tying sponges drenched in vinegar over their mouths and noses. During the work care must be taken lest the connecting-pipes, *c*, *d*, between the retorts and chambers get choked up.

In the bottom of the condensing chambers there is a pipe for running off the solution of ammonium carbonate, formed from the excess of moisture; here also a little steam escapes.

The product of this first operation is still very impure; at least if crude ammonium sulphate has been employed; it is in that case discoloured by tarry matters, and is sometimes sold as "ammonium carbonicum pyro-oleosum." It also mostly contains a little chalk or calcium sulphate carried over. According to Divers (p. 1315), whose observations have been confirmed by myself, this product has not the composition of commercial ammonium carbonate, no ammonia escaping during the distillation, but is normal ammonium carbonate $(NH_4)_2CO_3$, or, more probably, ammonium carbamate, $(NH_4)CO_2(NH_2)$. In case of a leaky and warm receiver, however, acid carbonate is formed, and the latter, that is, the commercial salt, is always produced in resubliming the first product.

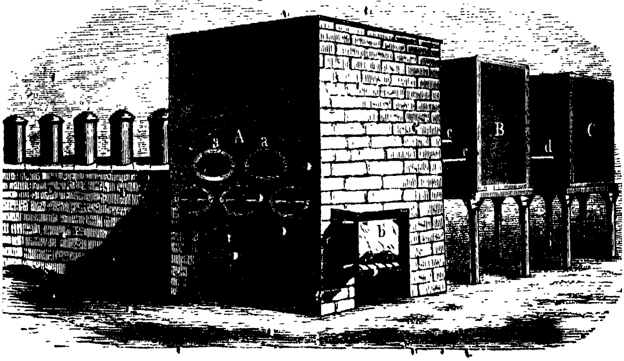


FIG. 335.

Resublimation.—This product, being too impure, is generally converted by resubliming into a white salt, forming fibrous transparent cakes 2 in. thick. This can be done, with hardly any expense, by the waste heat of the retort-furnace, which travels underneath a row of iron pots covered with cylindrical lead caps (shown at D in Fig. 335). The crude salt is put into the pots, along with a little water (without which the pure salt would not be transparent). Sometimes the pans are not exposed to the direct fire, but are placed in a common water-bath, heated by the waste heat of the retort-fire. A temperature of 70° suffices for resubliming; and it is best not to exceed this, because the salt turns out finer and less is lost by volatilization. The lead caps into which the salt is to sublime are made by rolling a sheet of lead into the shape of a cylinder, about 12 in. wide and 2 ft. 6 in. high, covering this at the top with a piece of sheet-lead, and pasting up the joints with paper. When the sublimation is finished, the lead is unrolled and the cake of salt can be taken out at once.

Another apparatus for resubliming[1] consists of an iron pan 2 ft. 6 in. wide at the bottom and 2 ft. at the top, 15 ft. long, and 2 ft. 6 in. high, in the cover of which there are eight 12-in. holes, on which are placed conical lead caps, 2 ft. 6 in. high, kept in their shape by clamps or wedges. With these it is possible to work fourteen days uninterruptedly. Then the clamps or wedges are loosened, and the mass is taken out; but it must be scraped off clean where it adheres to the lead. The salt is mostly packed in stone jars. Some liquid remains in the iron pan, most of which is left behind for the next operation.

The different qualities of white ammonium carbonate found in commerce seem to be obtained by heating more or less quickly, and by putting more or less water into the charges.

The *drying* of the ammonium bicarbonate is performed, according to the B. P. 9051, of 1915, and the Ger. P. 289300 of the Chemische Fabrik Brugg, by passing into the centrifugalled salt a sufficient quantity of ammonia and carbon dioxide at a pressure of 1½ atmospheres to form ammonium bicarbonate with the water present in the mass. The apparatus is constructed of aluminium or magnalium, and consists of an externally cooled chamber, provided with agitating-gear.

The usual process for making ammonium carbonate, as just described, does not appear to be quite rational. In the finished salt there is 1½ times (or, in the salt analyzed by Divers, 1¼ times) as much carbon dioxide as in the neutral salt; but according to the conditions of the process there is only enough CO_2 for the latter. Hence a large quantity of ammonia must go away in the uncombined state. This might be remedied by passing carbon dioxide into the subliming-apparatus; even an excess of this would not interfere with the formation of the ordinary ammonium carbonate.

(This suggestion, which was put forth in the 1882 edition of this work, has since been acted upon successfully by at least one manufacturer of carbonate of ammonia.)

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[1] Bell, *Chem. News*, xii., p. 303.

Other Methods for manufacturing Ammonium Carbonate.

Cedercreutz (*Chem. Zeit.*, 1915, p. 878) states that the Helsingfors gas-works recover ammonium carbonate directly from coal-gas, by condensing it in tents made of parchment paper, 2 ft. high.

Kunheim & Co., of Berlin, manufacture this salt in the most direct manner, by bringing together the gaseous mixture from the distillation of gas-liquor with carbon dioxide in lead chambers, thus producing the commercial salt.

Seidler (Ger. P. 26633) distils crude gas-liquor over limestone or dolomite, whereby the fixed ammonium salts are decomposed, so that the distillate contains, besides ammonium carbonate, only a little sulphide. This is removed by treating the concentrated aqueous solution with CO_2, and the commercial salt is produced from the precipitated crude ammonium carbonate by sublimation.[1]

F. C. Glaser (B. P. 5761, of 1884) heats salts of ammonia with equivalent quantities of sodium carbonate, to which a small quantity of bicarbonate has been added. The reaction is said thus to take place in a more perfect manner.

F. C. Teed (*J. Soc. Chem. Ind.*, 1885, p. 709), from experiments on a small scale, proposes running a solution of ammonium chloride slowly down a tower filled with small pieces of calcium carbonate, steam being blown up at the same time. Solid ammonium carbonate forms at the top.

Wächter (Ger. P. 34393) injects a spray of ammoniacal liquor, by means of a compressor, into a red-hot retort filled with calcium carbonate.

A method formerly employed by Kunheim & Co. consisted in subliming ammonium chloride with barium carbonate, to obtain barium chloride as a by-product.

Chatfield (B. Ps. 6751 and 6752, of 1888) decomposes ammonium sulphate by magnesia, and passes the NH_3 into water and CO_2 into this solution; when it shows 20° Bé. it is distilled with a further addition of CO_2, the distillate is freed from steam and the ammonium carbonate condensed.

H. R. Lewis (B. P. 14618, of 1895) passes waste gases from lime-kilns, blast-furnaces, etc., together with the gases from ammonia-stills, into condensers where crystalline ammonium carbonate is formed, the escaping NH_3 being condensed in a suitable manner. The carbonate is purified from sulphide by a current of air, or is washed and dried; or is converted into bicarbonate by CO_2 and moisture.

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[1] Details of the apparatus in *Dingl. polyt. J.*, cclii., p. 476, and *J. Soc. Chem. Ind.*, 1885, p. 112.

Raspe (Ger. Ps. 70977 and 83556) obtains ammonium carbonate directly from the products of dry distillation of coal, etc., by purifying them, before distillation, from sulphides and empyreuma by means of zinc carbonate and oil, then distilling in a column, heated to prevent obstructions, passing the vapours through heated towers filled with freshly ignited charcoal, and dehydrating by dry potash or soda. The ammonium carbonate is now condensed by cooling, and the remaining ammonia treated in the ordinary manner.

Saunders (U.S. P. 594100) describes his special apparatus for manufacturing ammonium carbonate.

J. Bueb and the Deutsche Continental Gasgesellschaft (B. Ps. 9177 and 22586, of 1910; U.S. P. 1004362; Ger. Ps. 237524, 246017, 252276) obtain solid ammonium carbonate by passing CO_2 and NH_3, together with the requisite quantity of steam, into a pipe heated to about 200°, that is above the decomposition temperature of ammonium carbonate, and causing the mixed vapours to solidify in a chamber, cooled from the outside to about 60°. Thus, it is stated, large quantities of a directly marketable product are obtained within a short time. According to their Ger. Ps. 285498 and 285531, the gases are passed in from below, and the sublimation-chamber is cooled on the top, but kept warm in its lower part.

The Chemische Fabrik Brugg (Ger. P. 286241) prepares in a continuous process a warmly saturated solution of ammonium bicarbonate, by conducting CO_2 into a solution of NH_3, in a column into which the NH_3 is passed at the top, and the CO_2 at the bottom. The column consists of a number of elements which are cooled in such a way that the temperature increases from the top downwards, and the liquor runs out at the bottom at a temperature of 50° to 60°, so that no crystals separate in the column, but only when cooling the liquor runs out of it. Their Ger. P. 289300 describes the conversion of centrifugalled into dry bicarbonate by treating it with

NH_3 and CO_2 in a cylinder provided with a revolving stirrer.

Hilgenstock (of the firm E. Bendel, of Magdeburg) manufactures ammonium carbonate directly from crude gas-liquor The first part of the apparatus is exactly like that used for manufacturing liquor ammoniæ; but the absorbing-vessels are constructed in such manner that at the same time CO_2 may be introduced into them, so that a saturated solution of ammonium carbonate is obtained. The worm within the absorbing-vessel can be filled either with steam or with cooling water. During the absorption of NH_3 and CO_2 it will be more frequently necessary to use cooling water. When the solution has got up to sp. gr. 1·40 (which corresponds to about 44¼ per cent. ammonium carbonate), steam is slowly passed through the worm, until the temperature of the solution has got up to about 70°. At this temperature commences the sublimation of ammonium carbonate into the condensing-chambers, which are made of lead, spread on a strong wooden frame. There are three such chambers, through which the vapours pass in succession; each of these may come first, or second, or third. The condensation of the vapours goes on in a very even manner. Towards the end of the process there is an excess of aqueous vapour which condenses in the chambers, forming a concentrated solution of ammonium carbonate which runs off from the inclined bottom of the chamber and goes back to the stills. When four or five still charges have been driven off, the chambers are allowed to cool completely; the doors of the first condensing-chamber are opened, and a workman, protected by a well-constructed hood, knocks off the salt inside the chamber with a wooden mallet. This product is already quite pure, and is sold after grinding it into powder. If required to be in the shape of lumps, it must be sublimed over again. This is done by means of cast-iron pots, covered with leaden hoods, and heated in a common water-bath up to about 75°, so that neither drawing in of air or blowing out of vapours can be noticed through the peep-holes in the hoods. After going on for about six days, the sublimed crust is about 1½ to 1¾ in. thick. The sublimation is now interrupted; when the hoods have cooled down the salt is knocked off with mallets or blunt chisels; any impurities on the outside of the lumps are scraped off, and the salt is now packed in tight casks, lined with parchment paper. It contains about 32·8 per cent. NH_3 and 52 per cent. CO_2. The non-condensed vapours in the last lead chamber are drawn by a steam-exhauster into a scrubber fed with water, for absorbing the ammonium carbonate which is used over again.

The Badische Anilin- und Sodafabrik (B. P. of J. Y. Johnson, 8763, 1914) pass NH_3 and CO_2 into a liquid not miscible with water, such as petroleum, solvent-naphtha, or the like, which is cooled at the ordinary pressure. Water may or may not be introduced at the same time. The CO_2 and NH_3 may be used in a pure or in a dilute state; in this way the various carbonates of ammonia can be formed and separate out in the solid state.

Kunheim & Co. (Ger. P. 250378) mix the components, CO_2, NH_3, and steam, intimately before admitting them to the sublimation chamber, whereby the formation of ammonium carbonate proceeds much more rapidly than by the usual method, and without the objectionable production of mist or fog.

A number of proposals have been made for obtaining ammonium carbonate in the manufacture of ammonia-soda, generally not for commercial purposes, but in order to be used over again; these are enumerated in Lunge's *Sulphuric Acid and Alkali*, 3rd ed., vol. iii., pp. 167 *et seq.* The results do not seem to have been very satisfactory.

Hempel (*Berl. Ber.*, xxi., p. 897) showed that ammonium carbonate (as well as chloride) can be reduced to hard lumps by compressing the powder very strongly at temperatures from 50° to 100° C. The process resembles the regelation of ice. It does not appear to be practically used.

Angelucci (*Gazz. Chim. Ital.*, vol. xlvi., p. 517) obtained ammonium carbonate by passing a mixture of acetylene and nitric oxide over platinum sponge, heated to 800° C., subsequently at once cooling down the gases to 100°. *Vide supra*, p. 1146.

Lennard (B. P. 5603, of 1904), in order to obtain ammonium carbonate free from lead, makes the sublimers and condensers of aluminium.

The *calcium-carbonate mud*, formed in the manufacture of ammonium sulphate by decomposing ammonium carbonate with calcium sulphate, is utilized by the Badische Anilin- und

Sodafabrik (Ger. P. 281174), which filters and washes that mud by means of a "dip- and aspirating-filter," to which it adheres in an even layer which admits of completely washing out the ammonium sulphate by a comparatively small quantity of water. Such a "dip- and aspirating-filter" is formed by a shallow wooden frame, covered on both sides with filtering-cloth, and provided with one or more openings for placing pipes therein.

Another process, described by the same firm in the Ger. P. application, B69749, consists in heating the calcium-carbonate mud and condensing the vapours evolved, which contain the ammonia in the form of carbonate.

Pure commercial ammonium carbonate (*cf.* its properties, pp. 1317 *et seq.*) is quite white, and at a fresh fracture shining and transparent, but is soon covered in the air by a fine dust of ammonium bicarbonate, ammonia being given off. On being heated it should volatilize completely and without empyreumatic smell; tarry matters are betrayed by a brown colour of the aqueous solution. The salt intended for analytical chemists should, after being neutralized with nitric acid, give no reaction with silver nitrate for chloride, or with barium salt for sulphate. Lime is indicated by a fixed residue and by precipitation with ammonium oxalate; lead (which should be absent when the salt is to be employed as a baking-powder) by means of hydrogen sulphide. Sometimes thiosulphate is found in it by dissolving in acetic acid and adding silver nitrate, which produces a white precipitate, turning brown in a few moments.

Applications.—This salt is principally employed for scouring wool, as a general detergent, in dyeing, as smelling-salts, as baking-powder, in medicine, etc.

Statistics.—No statistics on the manufacture of carbonate of ammonia are available, no more than for sal-ammoniac or the other salts of ammonia; the quantities of these salts are nearly always included in those of the sulphate.

In the German Empire there was:

Year.	Imported tons.	Exported tons.
1907	800	150
1908	673	139
1909	660	144
1910	774	195

AMMONIUM NITRITE.

Properties, *supra*, p. 1322.

This salt is sometimes employed in the manufacture of explosives and for the preparation of nitrogen. It can be prepared by double decomposition of lead nitrite and ammonium sulphate, as a crystalline mass, stable in the air. When slowly heated, it decomposes smoothly into nitrogen and water, $NH_4.NO_2=2H_2O+2N$; when quickly heated to 60° or 70° or by a blow, it decomposes with explosive violence.

Carez (Ger. P. 48278) manufactures it by reducing barium sulphate to sulphide in the usual manner and treating the solution with sodium nitrite. On evaporating the mixture and cooling, barium nitrite crystallizes out; the mother liquor is boiled with sulphur, to convert barium hydrate into sulphydrate, which is equally decomposed with sodium nitrite. The barium nitrite is then decomposed with ammonium sulphate.

Neogi and Adhicary (*J. Chem. Soc.*, 1911, xcix., p. 116) prepare ammonium nitrite by subliming a mixture of ammonium chloride and alkali nitrite in a vacuum. They did this only on a small scale, by means of a glass flask.

Bender (Ger. P. 280966) delivers water which has been treated with nitrogen and oxygen under pressure continuously to the porous walls of a closed, heated generator. The mixture of active oxygen and nitrogen thus produced forms ammonium nitrite when brought in contact with water. It may be used for sterilizing water or for converting sulphur dioxide into sulphuric anhydride or acid.

Ammonium nitrite is used in the industry of explosives, and for filling indiarubber balls, by a process described by Herbst.

AMMONIUM NITRATE.

The properties of this salt have been described, p. 1322.

Ammonium nitrate has recently become a most important material for the preparation of explosives, and is now manufactured on a large scale, by many methods which may be classed as follows:—

Production from ammoniacal liquor, preferably in the concentrated state, by saturation with nitric acid.

From other ammonium salts by means of nitrate of soda.

By oxidation of ammonia.

By the oxidation of atmospheric nitrogen. Since this presupposes the application of nitric acid, obtained synthetically from atmospheric nitrogen, we shall treat these methods lower down (p. 1572).

Production from Liquor Ammoniæ and Nitric Acid.

This simple method for obtaining ammonium nitrate is probably the oldest, and is employed up to the present time. Usually highly concentrated ammoniacal liquor is mixed with the calculated quantity of nitric acid in apparatus like that described *supra*, pp. 1527 *et seq.*, for the manufacture of ammonium chloride; the liquid is filtered and concentrated by evaporation up to the crystallizing point. The crystals obtained are drained by centrifugalling, and at once packed in air-tight casks, as the salt is very hygroscopic.

At Lille, according to *Mém. poud. salp.*, vii., p. 76, the State Gunpowder Factory employs gas-liquor of 22° Bé. and yellow nitric acid of 36° or 39° to 40° Bé., placed in stoneware vats holding 200 litres. The gas-liquor is run very slowly into the acid; if the vats are cooled from the outside, the liquor may be run in more quickly. The liquid is, before the acid is completely saturated, run into wooden vats, where it is allowed to cool completely, and is then neutralized by ammonia. Any sulphate present is removed by barium hydrate. The clear solution is concentrated in enamelled-iron pans up to 35° to 36° Bé.; before running it into the crystallizing-vats, 0·5 per cent. NH_3 is added, so as to make sure of obtaining a liquid containing no free acid. The liquid is stirred up from time to time during cooling, in order to obtain small crystals, which are dehydrated down to 2 per cent. water by centrifugalling.

Bühler, in *Chem. Ind.*, 1911, p. 210, describes the plant erected by him for the Norsk Hydro-Elektrik-Kvælstof-aktieselskab at Notodden (Norway) for the manufacture of ammonium nitrate, in which part of the nitric acid, obtained at that factory from atmospheric nitrogen by the process of Birkeland and Eyde (Lunge, *Sulphuric Acid and Alkali*, 4th ed. (1913), vol. i., pp. 232 *et seq.*), is worked up for this purpose, by means of liquor ammoniæ of 25 to 30 per cent. NH_3. The present production is 15 tons per twenty-four hours. The power required is 50 H.P.; twelve men are employed in that manufacture.

For working on a smaller scale, Guttmann (according to Escales, *Ammonsalpetersprengstoffe*, p. 24) recommends employing gaseous ammonia, liberated from ammoniacal liquor or from ammonium sulphate by means of lime, which is passed through a reflux-cooler, and then through a series of stoneware vessels, containing a layer of 15 to 20 cm. depth of nitric acid, sp. gr. 1·22. The neutral solution is forced through a filter-press and then evaporated in a lead pan, with conical bottom, at 120°, by means of steam of 5 or 6 atmospheres' pressure passing through a coil. The sufficiently concentrated solution is allowed to crystallize in wooden vessels lined with lead, or vessels of enamelled iron.

Garroway (B. P. 7066, of 1897) heats sodium nitrate with silica and steam; part of the nitric acid evolved is condensed; the remainder is made to meet NH_3 in plate towers, and the last NH_3 is retained by sulphuric acid.

Hake (*J. Soc. Chem. Ind.*, 1889, p. 106) proposes to make a very good product by allowing gaseous ammonia to meet with vapours of nitric acid.

Rudeloff (Ger. P. 166427) saturates the vapour of nitric acid, when coming out of the "steam column," for denitrating nitrous vitriol (Lunge's *Sulphuric Acid*, 4th ed., vol. i., p. 849) with ammoniacal liquor, spread over a large surface.

Of course, where the expense admits of it, liquefied ammonia, as it is sent out in steel bottles, may be used, allowing the gaseous NH_3 to pass into nitric acid.

Double Decomposition of Ammonium Salts with Nitrates.

Gerlach (Dingler's *Journ.* ccxxxiii., p. 82), in the year 1875, proposed dissolving sodium nitrate in the solution of ammonia, obtained by distilling gas-liquor, and passing carbon dioxide through the solution as long as any sodium bicarbonate is precipitated. The solution, remaining after filtering from the sodium bicarbonate, contains ammonium nitrate.—This process never had any practical application; the reaction is quite incomplete. Moreover, there was no sale for ammonium nitrate at that time. For the same reason the proposals of Lesage (Fr. P. of 20th Jan. 1877) and Chance (B. P. 5919, 1885) had no success.

To this class of processes also belongs that of Feld (B. P. 5776, of 1906; U.S. P. 839741; Ger. Ps. 171172 and 178620). He allows the gases of coal-distillation, after separating the tar, and removing the H_2S by a suspension of ferric oxide in hot water, or in other ways, to act on solutions of alkaline nitrates, in the "washers" constructed by him (p. 1197).

The ammonium salt, which is mostly used for conversion with alkaline nitrates, is the *sulphate*, the reaction being promoted by the great solubility of ammonium nitrate, and the much smaller solubility of potassium or sodium sulphate.

Roth (Ger. P. 48705) separates the products obtained by the interaction of ammonium sulphate and alkaline nitrates by means of alcohol. Or else (Ger. Ps. 53364 and 55155) he fuses equivalent quantities of ammonium sulphate and alkaline nitrate and heats to 160° or 200° C. for an hour, whereupon the liquid ammonium nitrate can be easily separated from the solid alkaline sulphate by centrifugalling or otherwise. But the same inventor later on (Ger. P. 149026) states that in this process about 20 per cent. of the sodium nitrate escapes the conversion with ammonium sulphate, and that double salts are formed which are very troublesome in separating the products of the reaction. He therefore now employs twice the proportion of sodium nitrate required by theory, or even more, say 132 parts $(NH_4)_2SO_4$ with 190 parts, or more, of $NaNO_3$, heating the mixed solutions, or mixing the solid salts and carefully fusing them under ordinary or reduced pressure.

Benker (Ger. P. 69148) mixes equivalent solutions of ammonium sulphate and sodium nitrate, and allows to crystallize in the cold, whereby much Glauber's salt is formed and removed. The mother-liquor is treated with sufficient nitric acid to form (with the sodium sulphate) sodium nitrate and free sulphuric acid; and by cooling it down ammonium nitrate is made to crystallize out. The mother-liquor is used over again.

Fairley (B. P. 1667, of 1896) mixes 132 parts solid ammonium sulphate with 170 sodium nitrate, adds a little water, and heats to 108° to 110°, at which temperature the mixture is kept for three to five minutes. It now consists essentially of ammonium nitrate and sodium sulphate, and is extracted with methylated spirits of 85 to 93 per cent., containing ½ per cent. NH_3. The alcoholic solution contains ammonium nitrate with 10 per cent. sodium nitrate, the solid residue sodium sulphate with 8 per cent. ammonium sulphate. The ammonium nitrate obtained from the alcoholic solution is purified by a special process. The mixed sodium and ammonium nitrates, after evaporation and recovery of the alcohol, are washed in an upright cylindrical vessel with cold water or a cold saturated solution of ammonium nitrate, which dissolves out the more soluble sodium nitrate. This process may be made continuous, and the moist ammonium nitrate, discharged from the top of the percolator, contains after drying less than 1 per cent. of impurities. The liquid from the percolator is evaporated to dryness, and the dry salts are used over again in the next operation, as well as the ammonium sulphate recovered from its admixture with sodium sulphate by treatment with boiling water.

The same inventor (B. P. 1668, of 1896; Ger. P. 97400) describes a new form of the ammonia-soda process, working at −15°, for the manufacture of ammonium nitrate. Another patent has been taken out by Groendahl & Landin (No. 1868, of 1892); but none of these, or the other alcohol processes, furnishes an article of sufficient purity for the manufacture of explosives, *i.e.*, containing less than 1 per cent. of solid impurities, as proved by Fairley (*J. Soc. Chem. Ind.*, 1887, p. 211).

Craig (B. P. 5815, of 1896; Ger. P. 92172) separates the mixture of ammonium nitrate and alkaline sulphates, obtained by the moistening of a mixture of alkaline nitrate and ammonium sulphate, stirring and drying, by means of liquid ammonia or most highly concentrated liquor ammoniæ, which dissolves only ammonium nitrate. For this he employs the apparatus shown in Fig. 336. An air-tight vessel, *a*, containing the filter *b*, is filled with the finely ground mixture of salts and digested, with the liquid ammonia contained in vessel *l*, at as low a temperature as possible. The filtrate may be brought to 80 per cent. ammonium nitrate, but it is safer not to exceed 50 or 60 per cent., to avoid contamination with other salts. It is run through into *e*; the ammonia is aspirated away by pump *d*, liquefied in *c*, and passed into *a* by means of pipe *f*, and this is continued until the mass in *a* is exhausted. The latter is freed from ammonia by heating, and the white ammonium nitrate discharged by the manhole *i*. The vessels must be very strong, on account of the high pressure, and should be made of iron, enamelled or coated with tin or aluminium.

Lennox (B. P. 5483, of 1897; Ger. P. 96689) heats a dry mixture of 17 parts sodium nitrate and 13 ammonium sulphate in a retort, connected with a condenser and a scrubber in a vacuum to such a temperature (not above 230°) that ammonium nitrate distils over, which commences at 200° C.; solid sodium sulphate remains behind. The retort is made of iron, the condenser of stoneware pipes. The vacuum is produced by an injector, and is made as high as possible. The nitric oxide formed during the process is liquefied (?) on issuing from the condenser. The gases are washed in the scrubber with a concentrated solution of ammonium nitrate. In order to prevent stopping up the condenser with solid ammonium nitrate, a steam-jet is passed through it. Similar to this is the process of Wahlenberg (B. P. 12450, of 1889).

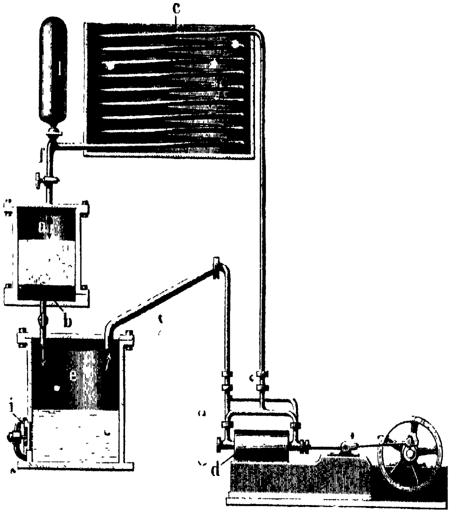


FIG. 336.

Johnson (*Chem. Zeit.*, 1897, p. 527; Swed. P. 8944, of 1897) converts calcium superphosphate by ammonium sulphate and ammonia into ammonium phosphate, which is converted into nitrate by the action of sodium nitrate.

E. Naumann (Ger. P. 166746) promotes the old reaction between ammonium sulphate and sodium nitrate by separating the sodium sulphate formed from the mother-liquor while still hot; the solution is then cooled to the point where only a double sulphate of ammonium and sodium crystallizes out, and the mother-liquor, on concentration and cooling, yields solid, nearly pure, ammonium nitrate.

According to his Ger. P. 259995, the mixture of ammonium nitrate and ammonium-sodium sulphate obtained in the fractional crystallization and by strong cooling of the mother-liquors is mixed with hot mother-liquors, relatively poor in ammonium nitrate, under such conditions that a solution saturated with ammonium nitrate at 25°-55° is obtained, from which, after removal of the separated double salt of ammonium sulphate and nitrate, ammonium nitrate is recovered by cooling to the ordinary temperature, with or without the addition of water. The double salt of ammonium sulphate and nitrate may be used in place of, or in addition to, the mixture of ammonium nitrate and ammonium-sodium sulphate, but in this case the treatment is first effected at 75°, at which temperature the double salt of ammonium sulphate and nitrate is decomposed. After removal of the separated ammonium sulphate, the further treatment is as described above.

The process of R. Wedekind & Co. (Ger. P. 184144; B. P. 19465, of 1906; Fr. P. 369389; U.S. P., of Caspari, Nydegger and Goldschmidt, 864513) runs quite on the same lines, but they add in the end so much water, that the sodium salts remain in solution, and only pure ammonium nitrate crystallizes out. They proceed as follows:—A solution is made of 400 parts ammonium sulphate and 720 sodium nitrate (= 40 per cent. excess) in 900 water, and is heated till it shows a boiling-point of 118°, at which point most of the sodium sulphate has been precipitated. The liquid is filtered and boiled down, until a sample cooled down to 70° begins to separate ammonium nitrate. It is then cooled down to about 70°, the salts separating thereby (sodium nitrate and sulphate) are removed and so much water is added to the mother-liquor that, on cooling down to 15°, the sodium salts remain in solution. The liquor thus diluted is cooled down to 15°, whereupon about 40 per cent. of the ammonium nitrate crystallizes out, free from sodium salts. The crystals are freed from the mother-liquor adhering to them by washing with a solution of ammonium nitrate. All the liquors go back to the next process.

Garroway (B. P. 10137, of 1899) first obtains strontium nitrate from sodium nitrate and strontium chloride (most of the NaCl separating out on cooling), and after purifying it by recrystallization, adds the exactly equivalent quantity of ammonium sulphate. The latter is thus converted into nitrate and remains in solution. All the strontium is precipitated as sulphate, which is converted into carbonate by means of sodium carbonate, and from the $SrCO_3$ the $SrCl_2$ is again prepared by means of hydrochloric acid. Carez (Ger. P. 42178) proceeds in the same way with barium chloride.

According to the German patent of the Norsk Hydro-Elektrisk Kvaelstofaktieselskab, No. 206949, of 1907 (*vide* p. 1562), ammonium nitrate is obtained, together with calcium nitrate, by absorbing nitrous vapours by calcium cyanamide, the reaction taking place quite smoothly according to this equation:—

$$CaCN_2 + 2H_2O + 4HNO_3 = Ca(NO_3)_2 + CO_2 + 2NH_4 . NO_3.$$

Burghardt (B. P. 8841, of 1889) mixes equivalent quantities of the solutions of lead nitrate and ammonium sulphate. Or else (B. P. 5542, of 1890) he precipitates the solution of lead nitrate with liquor ammoniæ, or saturates it with gaseous NH_3; the resulting white lead hydrochloride is to be converted into chrome-yellow.

Campion and Tenisón Woods (B. P. 15726, of 1890) decompose a solution of 85 parts sodium nitrate in 100 water by a solution of 62 ammonium chloride in 100 water, removing the NaCl formed. Or they decompose first the solution of 85 sodium nitrate in 100 water by a solution of 60 calcium chloride in 100 water, remove the sodium chloride, and decompose the calcium nitrate formed by a solution of 59 ammonium carbonate in 150 water, or 66 ammonium sulphate in 155 water.

Dyes (B. P. 15391, 1908) adds to a solution of calcium nitrate a solution of ammonium sulphate, so that calcium sulphate is precipitated.

Nydegger and Wedekind (B. P. 20907, 1909) state that manufacture of ammonium nitrate from calcium nitrate (which by its electrolytical production is a comparatively cheap starting-material) has the drawback that the commercial calcium nitrate contains various impurities, as alumina, ferric oxide, magnesia, and magnesium nitrate. When decomposing calcium nitrate by ammonium sulphate, the magnesium compounds enter into solution along with ammonium nitrate, and in the evaporation they are not removed, but remain in the crystallized ammonium nitrate, making this useless for explosive purposes. They avoid this by employing an excess of from 1 to 10 per cent. calcium nitrate (or barium or strontium nitrate), which causes the magnesium salts to remain in solution up to the last, after the crystallization of the ammonium nitrate, even in cases where 10 parts MgO or upwards are present for 100 NH_4NO_3. From the mother-liquor, the magnesia is recovered by an excess of ammonium sulphate in the shape of magnesium-ammonium sulphate. The same process is described in the Ger. P. 231394, of Wedekind & Co.

Plantz (Ger. P. appl. P30765) gives prescriptions for obtaining pure ammonium nitrate from crude calcium nitrate ("Norgesalpeter").

The Norsk Hydro-Elektrisk Kvaelstofaktieselskab (Fr. P. 408506) treat a mixture of the solutions of calcium nitrate and ammonia with carbon dioxide, producing a precipitate of $CaCO_3$ and a solution of ammonium nitrate.

The Gewerkschaft des Steinkohlen-Bergwerks Lothringen and F. Uhde (Ger. P. 254936; Fr. P. 417505) absorb the gases from coke-ovens, gas-retorts, etc., mixed with CO_2 if necessary, by a solution of calcium nitrate, with formation of ammonium nitrate and precipitation of calcium carbonate. This process, according to Fr. P. 436768 and U.S. P. 1053456, is modified by the employment of uncooled gases, without previous dehydration, at a temperature of the absorbing-liquid = 100°, by the use of concentrated ammonia gases, and acidifying the liquor obtained and heating until a reaction commences, whereby a chemically pure product is obtained. This proposal practically coincides with that of Walter Feld, laid down four years previously in the Ger. P. 171172 of Walter Feld.

Le Chatelier and Bogitch recommend decomposing calcium nitrate with ammonium sulphate at a temperature of 150°, because gypsum formed in the cold is in the shape of fine mud, difficult to wash. The crystals of gypsum are washed with boiling water, whereby ammonium nitrate free from calcium salts is obtained.

E. J. Henry (B. P. 19141, 1910) mixes calcium (barium, strontium) nitrate and ammonium sulphite solutions, preferably concentrated, in about equivalent quantities, and after separating from the precipitated calcium sulphite and removing any remaining calcium, if desired, by adding the calculated quantity of ammonium oxalate, evaporates the solution until it has a boiling-point of 125°, and then cools it to about 30°-40°, whereupon a large proportion of the ammonium nitrate crystallizes in a very pure state.

Colson (*J. Soc. Chem. Ind.*, 1910, p. 187) again proposes carrying out the ammonia-soda process by means of sodium nitrate, in lieu of sodium chloride, and thus to obtain large quantities of ammonium nitrate.

Knab (Fr. P. 116331) treats alkaline nitrates with ammonium oxalate.

Traine and Hellmers, Cologne, and Dr H. Weyer (Ger. P. 254935) heat calcium nitrate with an excess of ammonium sulphate, with or without addition of water, at ordinary or high pressure, up to the complete expulsion of the water and fusion, and lixiviate the resulting mass with an organic solvent which takes up only the ammonium nitrate, *e.g.*, alcohol. On concentrating, this solution ammonium nitrate of 99·9 per cent. is obtained, entirely free from lime, sulphuric acid, alkalies, and chlorine.

F. A. Freeth and H. E. Cocksedge (Ger. P. 256335) agitate equivalent quantities of ammonium sulphate and sodium nitrate with a hot solution previously saturated in the cold state with ammonium nitrate and sodium nitrate, and then with sodium sulphate, until the double salt of ammonium nitrate and ammonium sulphate begins to crystallize out, or with mother-liquors of the same composition, and evaporate the mixture as long as only sodium sulphate separates out; after removing this, the solution is mixed with water and cooled up to the point where ammonium nitrate crystallizes out. Their Ger. P. 271518 describes the production of ammonium nitrate from sodium nitrate and ammonium bicarbonate or its components, employing such proportions that at the end of the reaction, besides the precipitated sodium bicarbonate, a solution remains, saturated at the temperature of the reaction with sodium bicarbonate, ammonium bicarbonate, and nitrate; after removing the bicarbonates, the solution is cooled down and the ammonium nitrate now falling out is separated and washed in the usual manner. The most suitable temperature for the reaction is below 35°.

Wülfing, Dahl, & Co. (B. P. 26233, of 1913; Fr. Ps. 465683 and 466303) treat sodium nitrate (1 molecule), or a mixture containing other alkali or ammonium salts in aqueous solution with sufficient ammonium sulphate (at least 1 molecule), to convert all the alkali metal into alkali-ammonium sulphate, and separate the ammonium nitrate formed by fractional crystallization from the less soluble double salt, or concentrate the solution and extract it with alcohol or other solvent. Or they allow sodium nitrate and ammonium sulphate to interact in equivalent proportions, destroy the double salt by heating to 119°, concentrate the solution until most of the sodium sulphate has separated, and treat the mother-liquor as above, after adding more ammonium sulphate to convert the remaining sodium sulphate into double salt.

Menge, in a pamphlet published in 1915, discusses the preparation of ammonium nitrate, together with sodium bicarbonate, according to the equations:

$$(1)\ NH_3 + CO_2 + H_2O = NH_4 . H . CO_3$$

$$(2)\ NH_4 . H . CO_3 + NaNO_3 = NaHCO_3 + NH_4 . NO_3.$$

He obtained a conversion of 64·3 per cent. of the Na, and 63 to 70 per cent. of the NO_3, contained in the caliche employed.

Ammonium Nitrate by Oxidation of Ammonia.

We have in a previous place (p. 1333) mentioned the process of Ostwald for the oxidation of ammonia to nitric acid by catalytical means. This process has been carried out on a working scale at the Lothringen pit, near Bochum. According to information received from the Deutsche Ammoniak-Verkaufs-Vereinigung at Bochum their sales of ammonium nitrate made by the Ostwald process were as follows:—651 tons in 1908; 1096 tons in 1909; 1237 tons in 1910; about the same in 1911.

According to Traube and Biltz (*Ber.* 1904, p. 3130), the oxidation of ammonia by electrolytic oxygen in the presence of copper hydroxide, as catalyzer, into nitrite and nitrate is easily carried on, with large yields, in the laboratory, and it would probably also pay on the large scale.

Siemens and Halske (Ger. P. 85103) prepare ammonium nitrate by dark electric currents from gaseous ammonia.

Nithack (Ger. P. 95532) electrolyses for the same purpose water saturated with nitrogen under a pressure of 50 to 100 atmospheres.

Patents on the electrolytic production of ammonium nitrate from ammonia have been also taken by:—

Farbwerke vorm. Meister, Lucius, and Brüning, B. P. 16426, 1911; Ger. Ps. 223895 and 238137; Fr. P. 433410.

Elektrochemische Werke, Berlin, B. P. 16426, 1911.

Various Methods.

Hinselmann (Ger. P. 284641) obtains ammonium nitrate (or chloride), remaining white on keeping in stock, and free from sulphocyanide, by heating below the temperature of volatilization, whereby the sulphocyanide is converted into a black powder (persulphocyanide), from which the pure solution of nitrate (or chloride) can be separated by filtration. In the case of ammonium nitrate, the heating must be carried on at 135° to 140°, in that of ammonium chloride at 200° to 250°.

C. A. Woodbury, Assignor to E. I. du Pont de Nemours Powder Co., Wilmington, Del. (U.S. P. 1124679), prepares an explosive detonating at relatively low velocity, by incorporating ammonium nitrate in relatively large globular particles with nitroglycerin and an absorbent.

E. Collett and the Norsk Hydro-Elektrisk-Kvaelstofaktieselskab (B. P. 26697, 1912; U.S. P. 1058037) produce ammonium nitrate together with ammonium phosphate, by dissolving calcium phosphate in dilute nitric acid, adding ammonium sulphate in such proportion that the calcium is precipitated as sulphate, and treating the solution, which contains substantially only ammonium phosphate and nitrate, in any suitable manner, *e.g.*, by neutralizing with ammonia and fractionally crystallizing.

Steinmetz (U.S. P. 1062865) and Hlawaty (Fr. P. 453207) prepare ammonium nitrate and nitrite from steam and air in an electric furnace.

Statistics.

There are no statistics available on the production of ammonium nitrate. Rau (*loc. cit.*) states the German consumption of this salt at about 3000 tons.

Preparation of Granular Ammonium Nitrate.

Gallup and the Du Pont de Nemours Powder Co. (U.S. P. 1131361) evaporate the solution of ammonium nitrate in two superposed pans. If the temperature of the top pan is kept at 135° to 138°, the product obtained in the bottom pan is in a granular form. With a temperature of 150° in the top pan, the product comes out in a much coarser form, of which no more than 5 per cent. passes through a ten-mesh sieve. The grains are nearly globular and comparatively very little hygroscopic.

Examination of Ammonium Nitrate.

The commercial salt has nearly always an acid reaction. It is *qualitatively* examined by heating a sample in a platinum foil, where it ought to leave no residue.

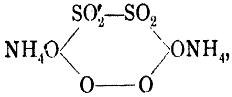
The *quantitative* examination is carried out for the percentage of *nitrogen*, which is carried out in a Lunge's gas-volumeter (p. 1276); and for *free acid*, which is titrated in the usual manner by caustic-soda solution. A red colour of the salt indicates the presence of *iron*, which can be estimated by the usual methods. The ammonium nitrate prepared by conversion frequently contains *alkaline sulphates* and *nitrates*, which remain behind on heating, and can be estimated in the usual way. The salt is very *hygroscopic*, and must therefore be tested for its percentage of *water*.

AMMONIUM PERSULPHATE.

Properties, p. 1321.

The salts of persulphuric acid, $H_2S_2O_8$, have recently found more and more applications for their oxidizing and bleaching properties. The most important of them is ammonium persulphate,

$(NH_4)_2S_2O_8$, or



from which the other persulphates are obtained by double decomposition.

Ammonium persulphate is always prepared electrolytically from ammonium sulphate. The conditions for this process have been studied by Berthelot (*Comptes rend.*, 1878, p. 20; 1880, pp. 269 and 331; 1891, p. 1418) and Elbs (*J. f. pract. Chem.* [N.F.] xlviii., p. 185). The monoclinic crystals of this salt are very easily soluble in water, 100 parts of which at 0° dissolve 58 parts; at 15° 65 parts of it (Marshall, *J. Chem. Soc.*, 1891, p. 777). The aqueous solution on heating is decomposed according to the equation:

$$(NH_4)_2S_2O_8 + H_2O = H_2SO_4 + O + (NH_4)_2SO_4,$$

with an evolution of + 38400 heat units.

The electrolysis is carried out with a saturated solution of ammonium sulphate at a temperature of 7°, and current density of 7 volt. The persulphate formed separates out in a solid form, and is filtered off from the mother-liquor, which must be neutralized with ammonium carbonate before going on with the electrolysis. The electrolysis of neutral solutions of ammonium sulphate has been simplified by working without a diaphragm, but with addition of solutions of chromates which allows the process to be carried out at 30°. The cathode is best made of carbon. The yield is depending on the state of the platinum anodes, smooth surfaces of the freshly ignited anodes acting favourably, rugged surfaces unfavourably.

According to the Ger. Ps. 155805, 170311, and 173977, of the Nürnberg Consortium für chemische Industrie, the yield of persulphate is essentially increased by adding fluorides to the electrolyte. According to another patent of that firm (Ger. P.

195811), the persulphate is produced by electrolyzing a saturated solution of ammonium sulphate, containing free acid, without a diaphragma, with a cathodic current-density of at least 20 amperes per superficial decimeter, without adding any chromium compounds (as had been previously done). The free acid must always prevail, so that even in the immediate neighbourhood of the cathode no layer with alkaline reaction is formed. The yield, which at 10 amperes per square decimeter is about 25 per cent., at 50 amperes rises to 50 per cent., at 150 amperes to 60 per cent., and at 300 amperes to 70 per cent. of the equivalent of the current. The process has the advantage of going on at a low temperature, without specially prepared electrodes and of yielding a product not contaminated by chromium compounds.

In the dry state ammonium persulphate is quite stable; in the damp state, as in damp air, it soon acquires an acid reaction, by being partially decomposed into normal ammonium sulphate, free sulphuric acid, and oxygen. The solution of the salt, when not absolutely pure, has a blue-violet fluorescence, and is slowly decomposed in the cold, more quickly on heating, like the moist salt, the oxygen mostly escaping in the ozonized form:

$$(NH_4)_2S_2O_8 + H_2O = 2NH_4 . HSO_4 + O.$$

The *application of the salt as an oxidizing agent* takes place in neutral acid or alkaline solutions. We mention the following applications. By heating it with a solution of aniline sulphate, aniline black is formed (Ger. Ps. 110249 and 105857 of the Badische Anilin- und Sodafabrik). Solutions of magenta are bleached in the presence of sodium acetate. Salicylic acid is oxidized into pyrocatechine, oxyanthraquinone into alizarine, alizarine into purpurine, alizarine bordeaux, and alizarine cyanine. The application of ammonium persulphate in photography is described by Eder and Valenta (*Chem. Ind.*, 1899, p. 197) and in the Ger. P. 79009 of the Chemische Fabrik auf Aktien vorm. E. Schering. Namias (*Chem. Zentr.*, 1900, ii., p. 806) reports on the application of the persulphates for oxidizing and bleaching purposes in the industries of weaving, dyeing, and bleaching. Peters (Ger. P. 96434) applies them as depolarizators in galvanic elements. Knorre describes their application as reagents; *e.g.*, "Caro's reagent" (*vide* p. 1576).

In pharmacy the persulphates are applied in small doses on account of their promoting digestion; they excite appetite, like the arsenites, but without the toxic action of these; larger doses may act lethally. According to Bifalini and Vitali (*Chem. Zentr.*, 1903, ii., p. 312), they are an excellent counter-poison in the case of poisonings by strychnine.

The *detection* of persulphate, according to Caro (*Z. angew. Chem.*, 1898, p. 845), is made by adding a 2 per cent. solution of aniline sulphate to a neutral solution of the salt, whereby an orange-coloured, crystalline precipitate is formed, which dissolves in hydrochloric acid with yellow colour, passing into purple on heating.

The *quantitative analysis* of the persulphate is mostly confined to the estimation of the active oxygen, which, according to Le Blanc and Eckhardt (*Zeit. f. Elektrochem.*, v., p. 355), is performed volumetrically by means of ferrous sulphate and potassium permanganate. To the solution of persulphate an excess of ferrous sulphate solution is added and the excess is retitrated by permanganate solution:

$$H_2S_2O_8 + 2FeSO_4 = Fe_2(SO_4)_3 + H_2SO_4.$$

The results are too low, if there is not a sufficient excess of ferrous sulphate present, or if the temperature is too low; at 60°-80° the reduction of the persulphate is instantaneous.

AMMONIUM PERCHLORATE.

Properties, p. 1325.

Alvisi (Ger. P. 103993) makes this salt by treating a concentrated solution of 273 parts of sodium perchlorate with a strong solution of 75 to 77 parts of ammonium nitrate. The ammonium perchlorate is precipitated in the form of small crystals, which are treated in a hydro-extractor or pressed, and then recrystallized.

Carlson (U.S. P. 985,724) mixes solutions of sodium perchlorate and ammonium sulphate, and allows the ammonium perchlorate to crystallize out at temperatures not below 22°.

Miolati (Ger. P. 112682) produces calcium perchlorate by the electrolysis of a solution of calcium chloride, and makes it act upon a concentrated, hot solution of ammonium chloride. For 55 parts $CaCl_2$, 54 parts NH_4Cl are required. On cooling, the ammonium perchlorate crystallizes out; it is filtered from the mother-liquor and purified by recrystallizing. The mother-liquor, containing $CaCl_2$, is distilled with lime, condensing the ammonia given off, and is again electrolyzed. The process goes on continuously, since only the NH_4Cl must be constantly renewed, but the $CaCl_2$ always returns into the cycle of reactions.

Ammonium perchlorate is employed for the manufacture of explosives. For this purpose also ammonium chlorate has been proposed, but Witt (*Chem. Zeit.*, 1910, p. 634) has shown that this salt is not manageable, whilst the perchlorate is less dangerous. The explosives made with it have been described by the names: permonite, jonkite, alkalite, persalite. They can be made non-sensitive against blows and friction. In the discussion on Witt's lecture (*loc. cit.*), Frank stated that in South Africa considerable quantities of perchlorates are made by means of water-power. The danger of explosion can be reduced, without stopping the detonating quality, by adding urea, guanidin, or diegaudiamidin. They are also employed along with nitrates, in which case the chlorine passes over into compounds, and the pit-air is not fouled by it.

Chlorates and perchlorates sometimes occur in commercial nitrate of soda, and are the cause of the poisonous action on plants sometimes observed when employing this as a fertilizer.

Concerning the *analysis* of ammonium perchlorate, the explosives' factories are very rigorous; they admit only traces of impurities, because these frequently enter into troublesome compounds with other constituents of the explosives. Most factories prescribe to the manufacturers their own methods of analysis. *Cf.* Lunge's *Technical Methods of Chemical Analysis*, translated by Keane (1911), vol. i., pp. 319-322, and vol. ii., pp. 484-485.

AMMONIUM PERBORATE,

$NH_4CO_3+3H_2O$, is produced by dissolving boric acid in a 2·5 per cent. solution of hydrogen peroxide, and precipitating the ammonium perborate by means of ammonia in the form of white, crystalline scales, which in the dry state are very stable.

AMMONIUM THIOSULPHATE.

Properties, p. 1321.

This salt, $(NH_4)_2S_2O_3$, is used to a limited extent for "fixing" the halogen compounds of silver in photography. It is usually prepared by passing SO_2 into a solution of ammonium sulphide, $(NH_4)_2S$. The following process is stated to yield a very pure technical ammonium thiosulphate.

The Chemische Fabrik auf Aktien vorm. E. Schering (Ger. Ps. 202502 and 202503) prepares that salt by mixing ammonium chloride (or sulphate or oxalate) with a concentrated solution of sodium thiosulphate, heating to about 100° C. and separating at this temperature, by means of a heated pressure-filter, the solution from the sodium chloride. A highly concentrated solution is obtained by introducing 60 parts of finely ground ammonium chloride into 150 parts of sodium thiosulphate, fused in its water of crystallization, and thoroughly stirring at a temperature of 95° to 100°. The salt collecting at the bottoms contains about 80 to 85 per cent. NaCl, and is separated from the liquid portion by means of a heatable pressure-filter. It is necessary to work at higher temperatures, because on cooling the equilibrium would be changed again, so that more sodium salt would remain in solution along with the ammonium salt. The concentrated solution, which contains about 42 per cent. ammonium thiosulphate and 17 per cent. sodium sulphate, is directly applicable as a photographic "fixing" bath, after diluting it for plates with 3 parts, for papers with 6 parts, of water.

If in the same way 248 parts crystallized sodium thiosulphate are stirred up with 132 parts finely ground ammonium sulphate, and passed through a pressure-filter, a filtrate is obtained from which, after adding 20 parts of water, no solid salt is separated on cooling. This solution has a sp. gr. = 1·41, and contains about 750 g. ammonium thiosulphate per litre. In this solution there are 4 molecules of ammonium thiosulphate to 1 molecule of the sodium salt.

AMMONIUM PHOSPHATES.

Properties, p. 1324.

Both the acid phosphate or monammonium phosphate, $(NH_4H_2PO_4)$, and the intermediate phosphate, or diammonium phosphate, $(NH_4)_2HPO_4$, are commercial products (*cf.* Th. Meyer, *Z. angew. Chem.*, 1891, p. 478, and T. H. Vogel, *ibid.*, p. 568).

According to Lagrange,[1] these salts are made from superphosphate, manufactured in the usual way by treating mineral phosphates with sulphuric acid. This product is lixiviated with water and with the aid of steam injected into the mixture, in a methodical way, whereby liquors of 25° Bé. are obtained. The residue, consisting principally of calcium sulphate, is thrown away. The solution contains free phosphoric acid, monocalcium phosphate, calcium sulphate, and a little free sulphuric acid. First the latter is removed by adding a slight excess of barium carbonate; the precipitated barium sulphate is separated by filtration and can be utilized as a paint. The filtrate, which now contains only phosphoric acid, monocalcium phosphate, and very little monobarium phosphate, is neutralized by ammonia in slight excess. This precipitates all the lime as basic phosphate, which is washed and used over again, along with the native phosphate, for manufacturing superphosphate. The filtered solution contains monammonium (acid) phosphate and will test about 20° Bé. It should be at that concentration, in order to effect the precipitation of the biammonium phosphate, in the following manner:—The above liquor and liquor ammoniæ (of 22° Bé.) are gradually mixed in small vessels, in the proportion of 1½ equivalents of NH_3 to 1 equivalent of monammonium phosphate. The biammonium phosphate at once separates out as a crystalline mass; but the vessels must be closed, to prevent the escape of ammonia, which is all the more likely to take place, as the reaction produces a rise of temperature. After cooling, the contents of the vessels form a thick paste, which is submitted to hydraulic pressure. The mother-liquor is used for the manufacture of ammonia; the cakes consist of pure $(NH_4)_2HPO_4$, and are sold to those sugar-refiners who employ the purifying process of Lagrange.

Washburn (U.S. P. 1115004) makes ammonium phosphate by adding gas-liquor to boiling hot crude phosphoric acid while bubbling steam through the acid, and continuing this for several minutes after the addition of the liquor, to remove volatile impurities. Detailed descriptions of his process are given in his U.S. Ps. 1142068 and 1151074; a modification in his U.S. P. 1167788.

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[1] Vincent, *Industrie des Produits ammoniacaux*, p. 104.

Bunte and Grahn (Ger. P. 47601) proposed to pass NH_3 from crude coal-gas directly into superphosphate, until this has absorbed 7 to 8 per cent. NH_3. But as such a product must contain sulphocyanides, which are injurious to the plants, the process does not seem to have found practical application.

According to the B. P. 26,726, 1908, and Ger. P. 220020, of N. Caro and T. E. Scheele, the employment of ammonium phosphate as a fertilizer up to that time had not been successful, because the product either contained too little nitrogen, or was too hygroscopic, or lost ammonia while being kept in stock or in transit. This is avoided by starting from crude phosphoric acid, as it is obtained by treating calcium phosphate with sulphuric acid, and which, besides phosphoric acid and dissolved salts, contains also free sulphuric acid. If ammonia is passed into this solution, a product is formed which keeps well in stock, which is easily spread out on the soil, and which contains about 65 per cent. of substances enriching the soil. The work is carried out in the following way:—Crude calcium phosphate is treated with sulphuric acid of 15° to 20° Bé., employing of this an excess of about 10 per cent. over that which is required for decomposing the phosphate, in order to produce a precipitate of calcium sulphate in the solid form. After separating this from the solution, ammonia is added to the latter until a slight excess is perceptible by the smell; the solution is then evaporated, and the residue, if necessary, dehydrated by drying. The product thus obtained contains 20 to 25 per cent. NH_3, and 40 to 45 per cent. phosphoric acid in the soluble form.

AMMONIUM CHROMATES.

Properties, p. 1324.

The normal chromate, $(NH_4)_2CrO_4$, is not of technical importance, but the bichromate or rather pyrochromate, $(NH_4)_2Cr_2O_7$, and the trichromate, $(NH_4)_2Cr_3O_{10}$, have been introduced into the manufacture of explosives. The *bichromate* forms easily soluble, garnet-red monoclinic crystals; lighted at one point, the salt is quickly decomposed all through with fiery glow, and leaves green chromium oxide. The *trichromate* is prepared from the former salt by the action of nitric or chromic acid. It forms dark red rhombic prisms, very easily soluble in water, with liberation of chromic acid; at 110° or 120° they assume a dark brown colour, and later on they deflagrate violently, leaving black chromium oxide.

The United States Smokeless Powder Co. (B. P. 10684, of 1894) prepares these chromates by mixing concentrated solutions of sodium chromates and ammonium picrate; the sodium picrate, which is very little soluble, is separated by crystallization.

Chromates in the pure state are obtained by electrolyzing the solution of an ammonium salt with employment of a diaphragm, and an anode consisting of chromium or an alloy of it. The application of such anodes can be avoided by employing some insoluble anode, if the electrolyte is a mixed solution of chromium sulphate and ammonium sulphate; care must be taken, by adding lime, to keep the liquid always in the alkaline state (Ger. Ps. 143320 and 146491).

AMMONIUM FORMATE.

Properties, p. 1325.

This salt has recently acquired interest since it has become possible to build it up synthetically from the elements. If a mixture of gases containing hydrogen, oxygen, and nitrogen, together with carbon monoxide (*e.g.*, the technical "water-gas"), is in the presence of a porous catalyzing agent exposed to dark electric discharges (*cf.* B. P. 2200, of 1903), at a temperature over 80°, formate is produced, whilst at temperatures below 80° only ammonia is formed. *Cf.* H. Pauling's U.S. P. 776543, and Ger. P. 157287.

According to Ger. P. 111078 ammonium formate is transformed by heating into oxalate. By adding some oxalate on the outset, according to Ger. P. 144150, this process is simplified and the yield increased. The same result is obtained, according to Ger. P. 161512, by the addition of alkali.

AMMONIUM ACETATE.

Properties, p. 1325.

W. Smith (B. P. 18693, of 1891) manufactures ammonium acetate from crude grey acetate of lime by dissolving this in a little water, settling, mixing the clear solution with more than its equivalent of a concentrated solution of sodium sulphate, filtering the solution of sodium acetate from the gypsum formed, evaporating to dryness, distilling the dry salt with sulphuric acid, neutralizing the distilled acetic acid with lime, evaporating the solution, heating the pure calcium acetate formed with a solution of ammonium sulphate to 60° or 80°, and separating the solution of ammonium acetate from the calcium sulphate.

According to B. Ps. 16093, 1890, and 5501, 1891, ammonium acetate may be employed in the manufacture of white lead. Considerable quantities of it are used in the manufacture of aniline colours, and in dyeing, in the place of caustic or carbonated alkali.

Ammonium Oxalate.

Properties, p. 1325.

The *neutral* salt, $(NH_4)_2C_2O_4+H_2O$, is found as such in Peruvian guano; it has no technical interest. The *acid* salt, $NH_4.HC_2O_4+H_2O$, is employed in photography, dyeing, and tissue-printing.

G. Muth (Ger. P. appl. M40486) dissolves alkaline oxalate in the solution of an ammonium salt, *e.g.*, of ammonium sulphate, and allows the solution to crystallize. Since sodium oxalate is much more soluble in solutions of ammonium salts, *e.g.*, ammonium sulphate, than in water, a certain excess of the ammonium salt must be employed in order to obtain a complete decomposition of the alkaline oxalate.

CHAPTER XVI

MANUFACTURE OF SULPHATE OF AMMONIA

IN several previous places of this treatise we have described the *direct* preparation of sulphate of ammonia from the products of the destructive distillation of fossile fuels (pp. 1175, 1196, 1204, 1208, 1214, 1236, 1239). In this chapter we treat of the manufacture of this salt from the ammoniacal liquor, obtained in gas-works, coke-works, and other industries.

Most of that ammoniacal liquor is worked for sulphate of ammonia. In Great Britain this has been done much earlier and on a vastly superior scale than on the Continent. In Germany it was hardly at all done before the year 1864, in which the firm of Vorster & Grüneberg erected a factory of ammonium sulphate at Kalk, near Cologne, which was very successful and led to the introduction of this industry in other places. But up to 1880 the production in Rhineland-Westphalia amounted only to 1250 tons, and very little indeed was made outside that district in Germany. Nowadays Germany has left Great Britain far behind, as we shall see later on.

The oldest way of preparing ammonium sulphate from ammoniacal liquor, which in some places producing small quantities of it is carried on up to this day, consists in the direct saturation of the liquor with sulphuric acid, and evaporating the solution down to the crystallizing point. This style of work yields a discoloured product, strongly contaminated with impurities, of which some, *e.g.* ammonium sulphocyanide (thiocyanate), greatly reduce its value as a fertilizer.

Another process, which has been carried out for many years past, makes use of the solutions of various sulphates of heavy metals, *e.g.* of iron and manganese, for purifying the gas from hydrogen sulphide, cyanogen, etc., and leads to obtaining the ammonia, present in the gas, in the shape of sulphate, crystallizing out on evaporation.

A further process consisted in bringing the ammoniacal liquor into contact with calcium sulphate (plaster of Paris) by means of filters or mechanical stirrers. The ammonium carbonate reacts on the calcium sulphate with formation of ammonium sulphate, remaining in solution, and of insoluble calcium carbonate, removed by filtration. But this process caused the loss of several other salts of ammonia, which do not react like the carbonate, and had to be abandoned.

Nowadays practically the only way of manufacturing sulphate of ammonia from the ammoniacal liquors obtained in the manufacture of illuminating-gas, coke, etc., etc., is the *distillation* of the liquor, which has been already described in detail in the last chapter. By this process the volatile compounds — free ammonia, ammonium carbonate, sulphide, sulphydrate, etc.—are driven off by the action of steam; and the non-volatile compounds—sulphate, sulphite, chloride, sulphocyanide, ferrocyanide, thiosulphate, and thiocarbonate — by means of heating with lime, furnish ammonia in the free state. The whole of the gases and vapours evolved, mixed with steam, are carried for absorption into receivers or "saturators," containing sulphuric acid of such a degree of concentration that, owing to the evaporation of water by the heat of neutralization, a crystallizing solution is formed, from which the solid ammonium sulphate, excreted in this way, is constantly removed. On one side the saturator receives constantly fresh sulphuric acid, as well as the mixture of gases and vapours from the ammonia stills; on the other side the solid ammonium sulphate is just as regularly taken out, and needs only drying to be fit for sending into the trade. The other constituents of the raw liquor, which have passed into the sulphuric bath in the shape of volatile compounds, mainly carbon dioxide and hydrogen sulphide, are driven out and carried away by the escaping steam. We shall give more details on this later on, when describing the saturators.

Apparatus for Manufacturing Sulphate of Ammonia.

The number of apparatus proposed, and even that which is actually employed, for working gas-liquor or other ammoniacal liquors is very great; a complete enumeration of them would not serve any useful purpose, and will not even be attempted in this treatise. Many of them are more or less unsuitable or quite obsolete.

Most of the apparatus mentioned below serve only for the production of sulphate of ammonia, but some of them answer equally well for preparing from gas-liquor, etc., a concentrated crude solution of ammonium carbonate and sulphide, for the use of ammonia-soda works or any other purpose, in order to save the comparatively excessive expense of carriage of the ordinary dilute gas-liquor. Some of them are also intended for making liquor ammoniæ, but this is best done by special apparatus, as described in Chapter XV.

We shall not detain ourselves with describing the simple boilers formerly in use, sometimes along with a sort of imperfect dephlegmating apparatus, but shall at once proceed to the description of apparatus more calculated to save fuel and labour. We begin with the older apparatus; after these we shall describe the more perfect continuously working stills.

Coffey Still.

We shall first, in Fig. 299, give a sketch of the combination of apparatus employed at a London works, where 100,000 gall. of gas-liquor are worked up per day, representing the product of 600,000 tons of coal per annum. The liquor arrives in canal-boats, A, and is pumped up by the pump *a* into a large settling-tank, B, where it remains for twenty-four hours. It is then pumped by the donkey-pump *b* into a "Coffey" still, C, 30 ft. high, 12 ft. long, and 5 ft. wide, into which steam of 2 atmospheric pressures is blown by five tubes. Here the volatile ammonium compounds are separated from the water and the non-volatile salts, which are usually run away into the canal because they contain only 3·5 per cent. of the NH_3, and, according to the view held in that place, do not pay for working off with lime. [This is an assertion frequently made, but probably quite erroneous.]

The volatile ammonium compounds pass out of the top of the still through a 2½-in. worm, perforated with numerous ½-in. holes, into the cylindrical saturator D, made of strong

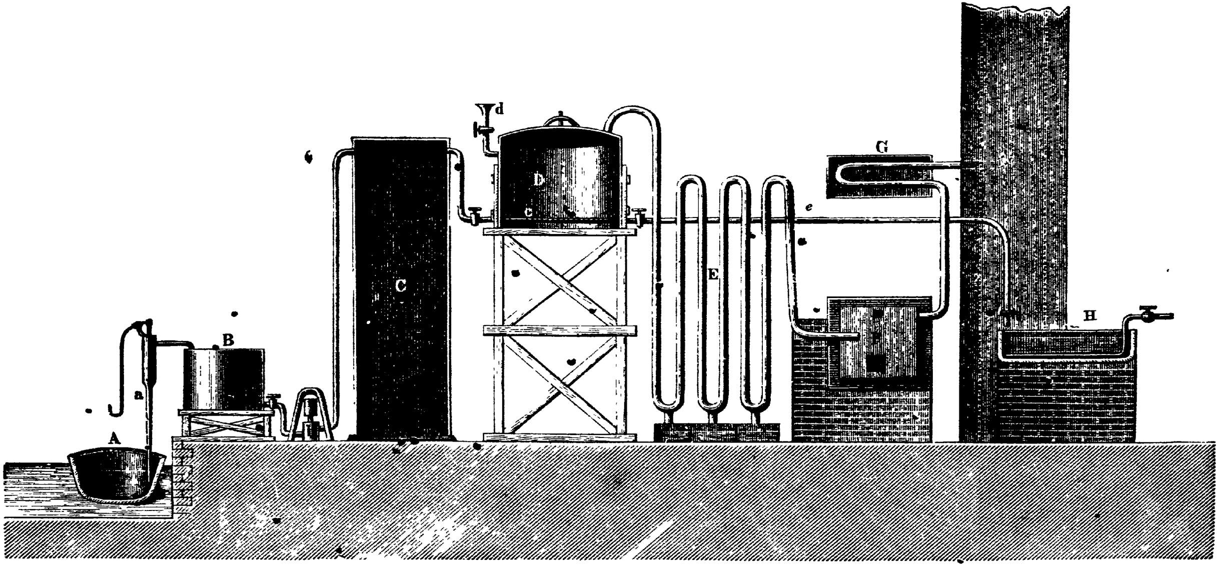

FIG. 299.

lead (20 lb. per superficial foot), the lower two-thirds being strengthened by strong planks bound with iron hoops. It is 6 ft. high, and 10 ft. wide, and is filled up to two-thirds of its height by means of the funnel-tap *d*, with a mixture of equal parts of sulphuric acid of 140° Tw. and water, which remains in the apparatus till it is completely saturated. The acid is purposely diluted, to prevent the salt from crystallizing within the saturator. When the saturation is completed—as witnessed by the liquor showing only a very faint acid reaction—steam is blown through for a quarter of an hour, to drive off all the sulphuretted hydrogen. The vapours evolved in this process and during the whole operation pass through the air-condenser E, to condense the moisture which is carried along, and then through a 7-in. metal pipe into the burner F. This is a square brickwork chamber, about 5 ft. wide, 8 ft. long, and 4 ft. high, loosely packed with firebricks, which are made red-hot before the commencement of the operation. Here the hydrogen sulphide takes fire, and is kept burning afterwards by its own heat. The hot gases pass through a steam-boiler (indicated at G), where their heat is partly utilized, and thence into a chimney, in which no smell at all of hydrogen sulphide can be perceived [but what becomes of the sulphur dioxide formed?]. The solution of salt is run from D through the pipe *e* into the lead pans H, 8 ft. in diameter, 2 ft. deep, made of 20 lb. lead heated by a steam-coil working at a pressure of two atmospheres. There is no smell perceived here. The ammonium sulphate crystallizing is fished out with a wooden spade, washed a little, and drained on a wooden floor. The mother-liquor serves for diluting the acid in the saturator. This process (*i.e.*, saturating with dilute acid and evaporating the solution) is preferred to the continuous running-in of acid and fisking-out of salts, because the result is more satisfactory.

Coffey's still was originally constructed for rectifying spirit of wine, but has been employed for many similar purposes—for ammonia first by Newton, in 1841. Fig. 300 represents the shape employed for spirit of wine: that employed for ammonia is essentially the same; but wood lined with lead is substituted for copper. It consists of an oblong vessel B, and two superposed columns, CDEF and GHIK. The former is called the analyzer, the latter the rectifier. The latter is made of 6-in. wood lined with lead, so that little heat is lost by radiation.

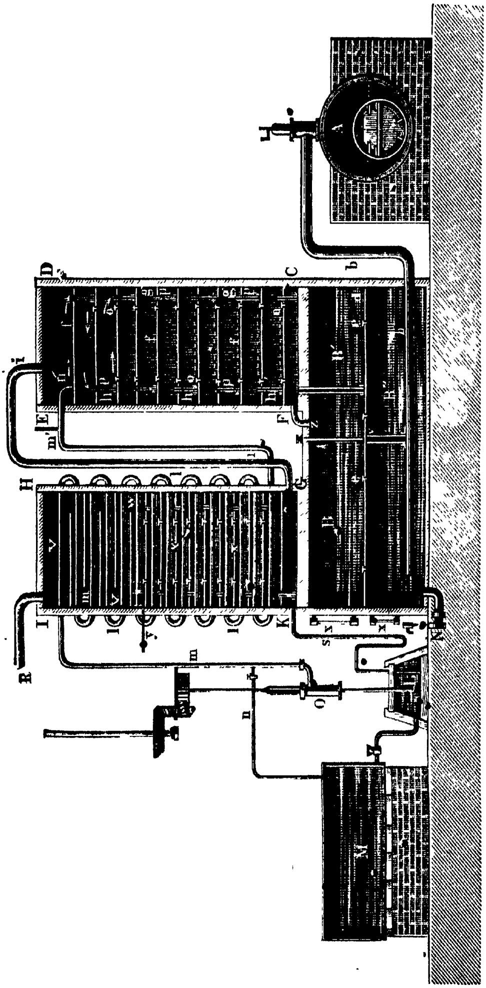

FIG. 300.

B is divided into two chambers, B′B″, by the horizontal diaphragm *d*, which is perforated with numerous apertures for the passage of the vapour, and is, moreover, furnished with several valves opening upwards, *e e*, in case of more vapour being given off than can escape through the apertures. A pipe, *v*, reaches nearly to the bottom of B″, where it dips into a hydraulic lute; it can be opened or shut off by a valve attached to the rod *t*, which passes through a stuffing-box at the top. *x x* are liquor-gauges for B′ and B″. The *analyzer* CDEF is divided into twelve chambers, *f f f*, by sheet-iron diaphragms, *g h*; these also contain many perforations, as well as valves opening upwards, *o o*; also overflow-pipes, *p*, projecting about an inch above each plate, so that a corresponding depth of liquid always remains on each diaphragm. The pipes *p* reach down to the next lower diaphragm, where they dip into hydraulic lutes (traps), so that no steam can escape through them; they are inserted at alternate ends of the diaphragms.

The *rectifying-column* GHIK is in a similar manner divided into fifteen chambers. The lower ten of these are filled exactly like those of the analyzer, their diaphragms being furnished with perforations, valves, and overflow-pipes. The top chamber of these ten is covered by a metallic diaphragm, with only one large opening at *w* for the passage of vapour, and an overflow-pipe *s*. *w* is surrounded by an upright flange, which prevents the return of the most rectified liquid into the lower part of the column. *s* is closed by a hydraulic trap of much greater depth than the others, from which a pipe, *y*, carries away the condensed but still very hot liquid into a worm or other refrigerator.[1] The upper five chambers, *v*, are formed by plain unperforated diaphragms, with openings at alternate ends large enough for the passage of both vapours and liquid; their only use is to cause the vapour to pass along the pipe *m* in a zigzag direction, so as to enlarge the cooling-surface. The pipe *m* runs through all the fifteen chambers in a zigzag, as shown in Fig. 301, the bends *l l* (Fig. 300) forming the connection between the pipes of the different chambers, thus constituting one continuous pipe leading from the pump O upwards, then downwards through all the chambers of the rectifier, again rising upwards outside, and finally ending in the analyzer at *n*′. M is the store-tank for the liquid to be rectified; L, the well for the pump O, which is working continuously, and supplies rather more liquor than is necessary to keep the apparatus going; the surplus runs back into M through a pipe, *n*, furnished with a stopcock by which the operation can be exactly regulated. The necessary heat is supplied by the steam from the boiler A; the steam-pipe *b b* within the receiver B″ branches into a number of smaller perforated pipes (these are not shown in the diagram).

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[1] This can be omitted in rectifying gas-liquor, except when liquor ammoniæ is to be made in the apparatus itself.

An operation is commenced by setting the pump O in motion, till all the zigzag pipes, *m m*, are filled and the liquor passes into the analyzer at *n′*. The pump is then stopped, and steam is let into the still through *b b*; it passes up through the receivers B″ B′, then through the pipe *x* into the analyzer, passes into *i*, in which it descends, and enters the bottom of the rectifier at G. It then rises through the chambers X X, surrounds the zigzag pipes, and heats the liquor in them. When the attendant by feeling the bends *l l* perceives that perhaps eight or ten of the chambers of the rectifier have become heated, he again sets the pump to work. The gas-liquor, now nearly boiling-hot and always in rapid motion, flows from *n′* into the analyzer and downwards in this through the overflow-pipes *p p* from chamber to chamber, as shown by arrows in the top chambers. It cannot pass down through the perforations of the diaphragms, whose number and size are so regulated that they are only just sufficient to afford a passage for the vapours upwards when under some pressure. Steam and vapour thus pass in each chamber in numerous jets through a thin stratum of liquor, and so completely expel all volatile ammonium salts that in B no trace of these can be found. When the water-gauge *x* shows that B′ is nearly full, the valve at *t* is opened and the contents of B′ are discharged into B″. When this is also full its contents are discharged by the tap N, the contents of B′ are again run into B″; and in this way the process goes on, so long as there is any liquor to be distilled. The boiling-hot spent liquor running from B′ serves to raise the temperature of the water intended for feeding the steam boiler A.

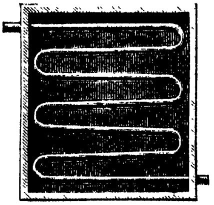
FIG. 301.

Having now followed the liquor in its course onwards to the point where it is deprived of all volatile ammonia, we will trace the course of the steam. This in its passage through the twelve chambers of the analyzer takes up a large quantity of ammonia, and is partly condensed to water. The remaining mixture of steam and vapour at *i* passes into the rectifier, surrounds the pipes *m m*, heats their contents, and by condensation parts with more of its watery portion, which condenses in a boiling state on the various diaphragms. What escapes through *w* is nearly pure ammonia; and this, after being further cooled in *v v* and having lost the last portions of water, escapes through R into the saturator D, Fig. 299.

If liquor ammoniæ is to be made, the gas-liquor must be mixed with lime. In this case less steam is blown in, so that the chambers *v v* remain at the ordinary temperature, and from the pipe *y* strong liquor can be obtained at will, passing at first, by preference, through a refrigerator. The water condensing lower down in the rectifier contains a little ammonia, and hence runs back through *s* into L, in order to be pumped up again by O.

The operation is mainly regulated by observing the thermometer *m'*, which shows the temperature of the liquor issuing from *n'*. Whenever the liquor is too hot, more liquor is let into the apparatus, or *vice versâ*, which can be effected at will by the overflow-cock *n*.

According to the requirements of certain works, Coffey stills are made more or less wide and high, with a corresponding number of steam-pipes and chambers. Such stills hardly pay when less than 10,000 gall. of liquor are worked up per day.

Sometimes they are made much less elaborate than is shown in the above description, plain shelves (up to sixty in number) springing from opposite sides of the tower, and being so made as to retain upon them a thin layer of liquor, the excess of which runs over the free edge of one partition to the next partition below it, and so on to the bottom. Something like this has been patented by Brullé and Leclerc (B. P. 1086, of 1880).

At one ammonia-works the Coffey stills are from 18 to 25 ft. high, 6 to 10 ft. long, and 1 or 2 ft. wide, with 20 or 30 diaphragms, 3 in. apart; at the top there is a space of 6 in., at the bottom another of 2 ft. (in lieu of the receiver B, Fig. 300). Steam of $1\frac{1}{3}$ to 2 atmospheres is employed. The liquor used in this works is 7½° Tw. strong; the solution of ammonium sulphate is boiled down to 52° Tw. before it is allowed to crystallize.

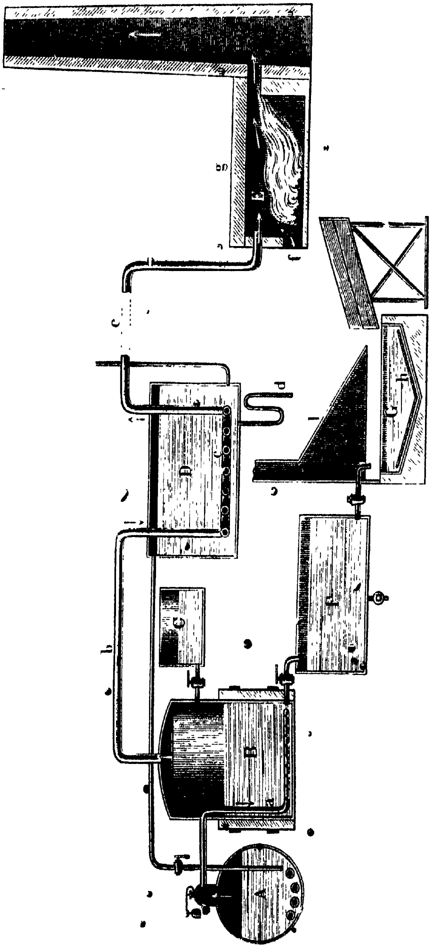

FIG. 302.

Horizontal Cylindrical Stills.

At another ammonia-works the gas-liquor is distilled in *horizontal cylindrical stills*, A (Fig. 302), holding 10,000 gall., and charged with 7000 gall. each time. The heat is applied by somewhat superheated steam in a closed coil. It is preferable to employ gas-liquor of not less than 5° Tw., or, say, 10 oz., without addition of lime. Experience has shown that the loss, including the fixed ammonia, is always 1 oz. per gallon; so that from a 16-oz. liquor, sulphate equal to 15 oz. is obtained (?). The vapours issue through a lead coil, *a*, perforated with ¼-in. holes 6 in. apart, into a lead saturator, B, strengthened by planks and hoops. This is charged with sulphuric acid of 47° Tw. from the tank C, which is filled by means of an air-pressure apparatus (acid-egg).[1] The vapours escaping from B pass through the 8-in. pipe *b* into the closed vessel D, where they circulate in the coil *c*; the liquid condensate runs away at *d*. D is filled with gas-liquor, which is thus heated and serves for feeding A. From D the vapours issue at *e*; they are now cooled by air through travelling round the works in a pipe 300 ft. long, in which nearly all the water condenses, and are at last conveyed into the furnace E, where a fire is kept up with small coal. Air enters at *f*; and the combustion of the hydrogen sulphide is completed by causing the gases to pass along the red-hot arch *g*. The sulphur dioxide escapes into the air.

The solution of ammonium sulphate from B runs into the settler F (9×9×2 ft.), and from this, through a tap, 4 in. from the bottom, into the boiling-down pan G (20 ft. long, 5 ft. wide, 2 ft. deep, half of this being straight, half conical). The heat is applied by means of the steam-coil *h*; the vapours pass away by the hood I.[2]

Continuous Saturation Apparatus.

Fig. 303 is a sketch of the apparatus in operation at a large London works, where lime is employed and where *continuous saturation* is preferred. The gas-liquor is pumped at *a* into a column, B, which it traverses from the bottom to the top in many pipes, the empty space being filled by the hot gases from

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[1] *Cf.* Lunge's *Manufacture of Sulphuric Acid and Alkali*, vol. i., 4th edition (1913), pp. 814 *et seq.*

[2] An exact description and diagrams of the steam-heated concentrating-pan, merely sketched here, is given in Lunge's *Manufacture of Sulphuric Acid and Alkali*, 4th edition, vol. i., pp. 1098 *et seq.*

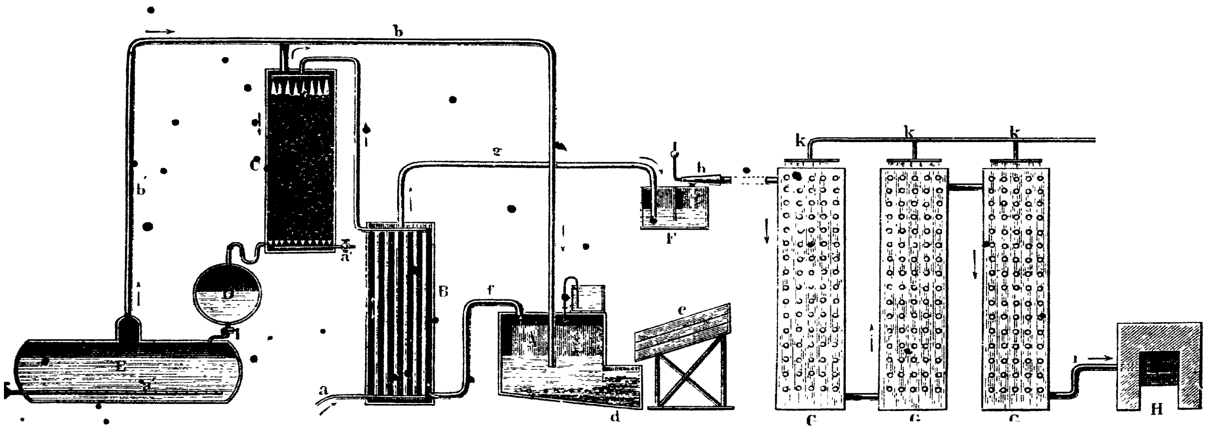


FIG. 303.

the saturator A, which thus raise the temperature of the liquor. The latter now passes into a square iron column, C, about 3×3×20 ft., packed with retort-graphite. In this the gas-liquor descends, whilst steam enters through *a'* and expels the volatile ammonium salts, which escape at *b*. The liquor passes into D, a small reservoir intended to feed the horizontal still E, in which it is mixed with lime; the steam let into this effects both the agitation and the distillation. The vapours escape at *b'* and unite with those from *b* before passing into the saturator A. This is a large lead vessel, continually fed with a thin jet of sulphuric acid of 140° Tw. It is adjoined by the box *d*, open at the top; the partition does not reach quite to the bottom, but is always kept luted by liquid. The sulphate of ammonia at once separates in a solid form, is raked out on the sloping bottom of A into *d*, fished out with perforated spades, and drained on the drainer *c*. The mother-liquor always runs back into A; the drained salt is at once sent into the market. The hot mixture of steam and gases, escaping from A, first passes through *f* into B in order to heat the gas-liquor (as mentioned above), then through *g* into a vessel, F, where it is forced through water by a Körting's blower, *h*, and is thus washed and cooled. The complete cooling and condensation of the steam, which would otherwise be a drawback in burning the hydrogen sulphide, is effected in the columns G G G, pierced by numerous pipes, passing right across, so that abundant air-cooling takes place; and the liquid can run off below. In summer cold water is run upon these columns from the pipes *k k k*. The cool and dry gas is conveyed by *i* into the furnace H, where it passes through a coke fire, with access of air, and where H_2S is burned into SO_2, as in the former case.

This apparatus seems to be one of the best of the older forms. Each set as described is equal to the production of 100 tons sulphate per week. Recently the burning of the hydrogen sulphide has been given up, and it is, instead, absorbed in ordinary oxide of iron purifiers, which, however, do not appear to give full satisfaction.

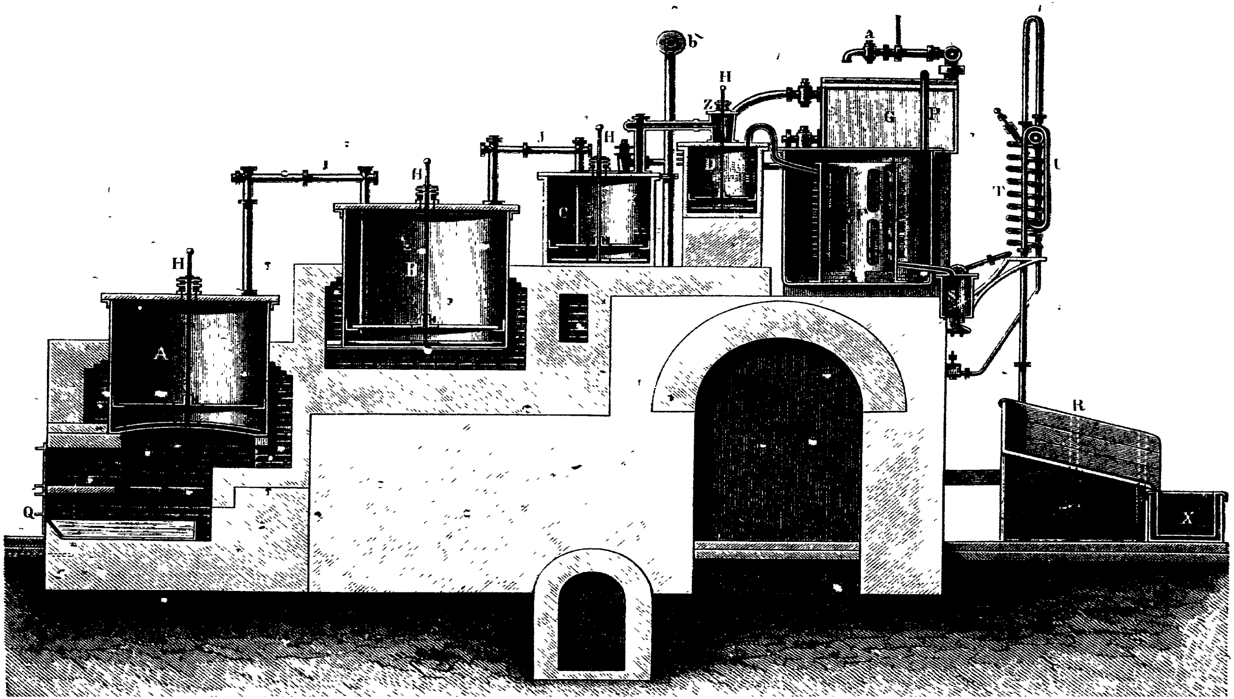
Dutch Apparatus.

At a Dutch works I saw the following apparatus:—Three horizontal cylindrical boilers are worked in a set The first two of these receive milk-of-lime, but this is only pumped in after most of the volatile ammonia has been expelled. The gases and steam pass through the third boiler and then into the saturator, which is of the usual form. The hydrogen sulphide and other noxious gases, given off in the closed part of the saturator, are conducted away in a pipe and are cooled down, first by cold ammoniacal liquor, then by cold water, whereupon they are passed into a small coke fire, above the grate, in order to be burned. The whole saturator, including the open part, is covered by a large wooden hood, from which a pipe leads to the high chimney, so that there is no stench even from the open part of the saturator. The acid used is = 60° Baumé (sp. gr. 1·71), and the fished-out salt is dried on iron plates, heated from beneath.

Apparatus of A. Mallet.

This apparatus was constructed as early as 1841, but a number of them were still at work at the time of my visit at the ammonia-works belonging to the Paris Gas Company, which proves that it must be one of the most serviceable forms of the older type of ammonia-stills. It is represented in Fig. 304 in longitudinal section, in Fig. 305 half seen from above, half ground-plan, in Fig. 306 back elevation. It consists of two sets of three stills each, A, B, and C, holding above 1000 gall. apiece, A and B being heated by direct fire. They are provided with agitating-gear, H H, passing through glands in the covers, for mixing the gas-liquor and lime and for preventing any burning on. C serves for washing the vapours from B, and is at the same time heated by these. From D the vapours enter a worm, about 70 or 80 ft. long, placed in the tank F and cooled by gas-liquor. The liquid here condensed flows into S, and thence into the collector Y. The gases leave the upper part of S and pass through an air-cooled worm, T, through the pipes U (provided with a safety-apparatus), and into the absorbing-vessel V. The products condensed in T run back into Y.

The gas-liquor, freed from tar, is drawn through the tap *a* into the measuring-vessel G, which at the bottom is connected by a tap with the cooler F; a pipe, branching off at the top, leads to the milk-of-lime pan E. The vessels A, B, C, D are


a
b
H
Z
H
G
F
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D
U
J
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A
S
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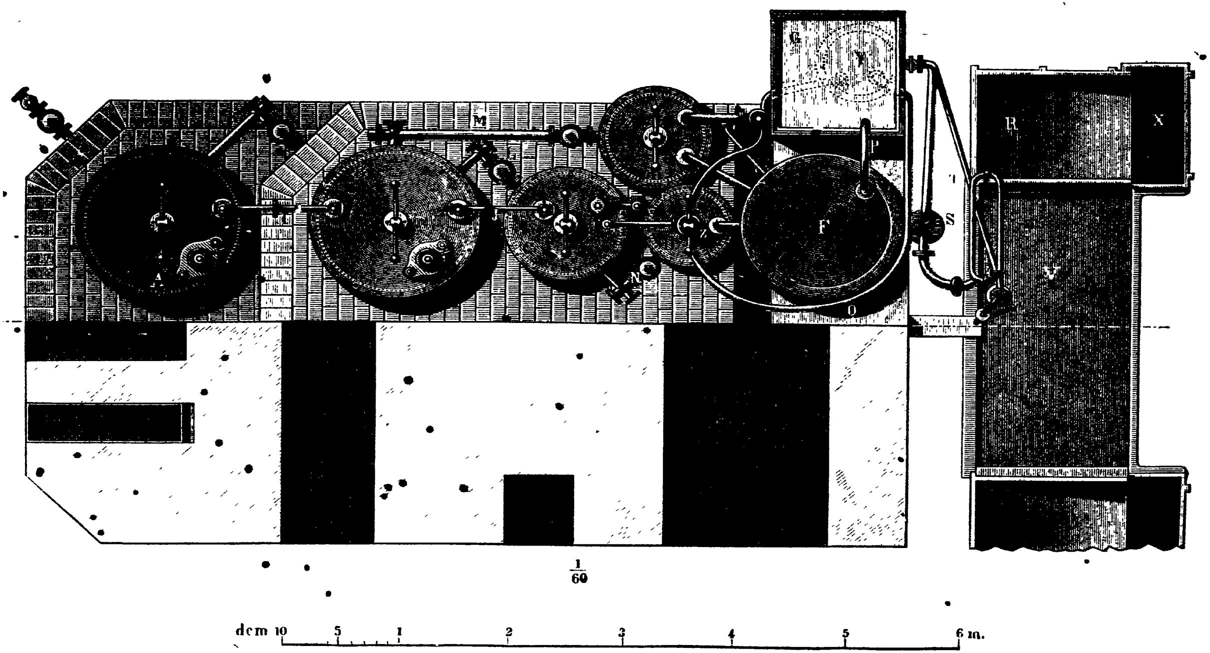

FIG. 305.

connected at the bottom by the pipes K, L, N, and at the top by the pipes I, J, which reach nearly down to the bottom of B and C. The pipe M takes the milk-of-lime from E into B. Through the pipe O the contents of the vessel Y can be emptied into the vessel D. The pipe P carries to G the vapours given off in the cooler F. Z is a three-way cock, by which the pipes connected with D can be alternately put into communication. In Q is the fire, which first travels round A and then underneath B. R R are lead-lined wooden drainers for the ammonia-salts. X is a leaden tank for the mother-liquors, which go back to V.

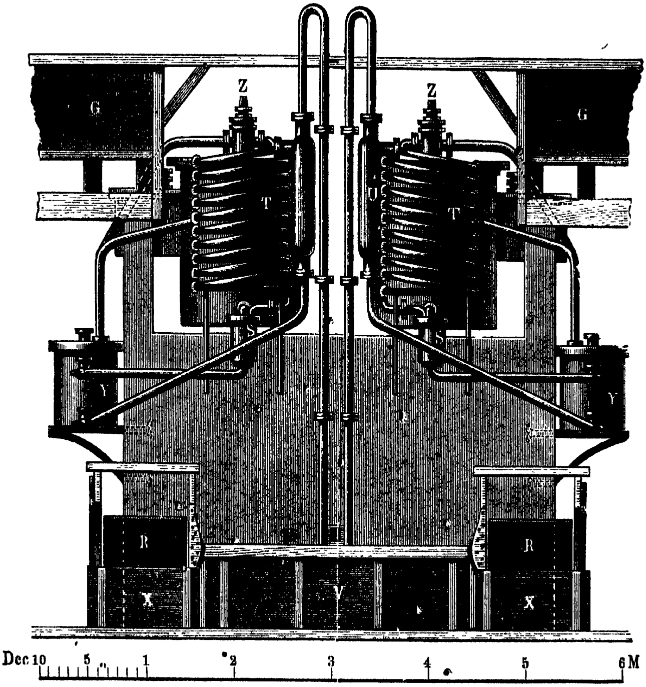

FIG. 306.

The saturators are usually made of wood and lined with lead; the ammonia-gas issues through a horizontal lead pipe, lying at their bottom, into the acid or the water. The saturator has an air-tight cover; and the non-condensed gases escape through a pipe into the fireplace of a steam-boiler, in order to be burned.

If caustic ammonia is to be prepared, before distillation a quantity of lime sufficient for decomposing all the ammonium salts must, of course, be put into the still, to avoid contamination of the product. For making ammonium chloride or sulphate much less lime is required; and sometimes none at all is employed, the small quantity of fixed ammonium salts being given up as lost. The liquor ammoniæ obtained is only of the crude amber-coloured quality.

In actual practice only a small portion of the gas-liquor in E is mixed with lime, half an hour before the operation; most of the liquor is run from G into F, where it serves as a refrigerant and is itself heated in the process; for this purpose it enters the vessel at the bottom and leaves it at the top. The stills are provided with safety-valves and water-gauges. At the end of the process the liquid is run away into a main drain.

The worm in F is 2 in. wide and has nine coils. The worm T, when, instead of liquid ammonia, ammonium sulphate is made, is replaced by a cylinder 10 ft. high and 4 ft. 6 in. wide, into which the gas-delivery pipe from S enters and passes down nearly to the bottom. This cylinder is kept about one-third filled by means of an overflow-pipe shaped like an inverted siphon; the overflowing liquid is collected in Y, like that coming from S. From that cylinder the gas passes first through an iron pipe, provided with a Welter's safety-tube to prevent any liquid from being forced back by atmospheric pressure, and then into a large lead tank, into which it issues from two lead pipes, lying at the bottom and perforated by many holes. The tank is two-thirds filled with sulphuric acid of 53° Bé. = 116° Tw.,[1] and provided with a roof-shaped cover, from which the escaping gases (carbon dioxide and hydrogen sulphide) are carried into the chimney by means of a wood conduit. The sulphate crystallizing out is fished out from time to time, drained on sloping lead plates, and dried in a stove or upon metal plates heated by some waste heat.

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[1] Where such acid is employed, the temperature of the entering gas must be 80° if the sulphate is to crystallize out continuously.

As soon as a sufficient quantity of liquid has collected by condensation in the vessels Y (say once an hour), the three-way cock Z is for some minutes adjusted so that the gas from D passes no longer into the worm F, but into Y (this is best seen from Figs. 303 and 304). Its pressure forces the liquid from Y through O into D; so that no pump is needed for this. The pipe O must reach down to the bottom of Y. Every three hours the contents of A are run off, and those of the succeeding stills B, C, and D are run a stage lower down.

Each apparatus is charged with 12 hl. (say 270 gall.) of liquor, and six operations are made in twenty-four hours, with an expenditure of about 12 hl. of coke as fuel in twenty-four hours, and of 130 litres of slaked lime for each charge of 1200 litres of liquor. Each cubic metre (or ton) of gas-liquor of 3°·5 Baumé (=8°·5 Tw.) yields 70 kg. of sulphate; each apparatus yields, therefore, about 500 kg. of sulphate per twenty-four hours.

At La Villette at the time of my visit a daily quantity of 10 tons ammonium sulphate was manufactured in ten double Mallet's apparatus, and 5 tons liquor ammoniæ in four apparatus.

A drawback of this apparatus is, that no proper provision is made for dealing with the hydrogen sulphide; it also contains a number of unnecessary complications, and is undoubtedly inferior to the modern steam-stills of Grüneberg and Feldmann.

A. Mallet later on improved his apparatus by replacing the worm-condensers by upright tubular condensers, similar to those shown in the benzol rectifying-apparatus, Figs. 189 and 196 (pp. 909 and 926), and by the addition of a rectifying-column, similar in principle to those in use for spirit of wine, etc. *Cf.* also p. 1400.

Grüneberg's Apparatus.

For the general principles of this, we refer to pp. 1347 *et seq.*, where his apparatus for concentrated gas-liquor is described.

The apparatus, Fig. 307, serves for producing ammonium sulphate. The gaseous mixture passes through *k* and alternately through *k'* and *k''* to the saturators K' and K'', containing sulphuric acid. Considerable heat is evolved by the combination of this acid with ammonia, so as to vaporize the excess of water present in the acid [provided the latter be not much under 130° Tw.]. The vapour thus generated, together with offensive gases (CO_2,H_2S, etc.), pass along the large pipe *u* and into the vessel E, where their heat is utilized for a preliminary

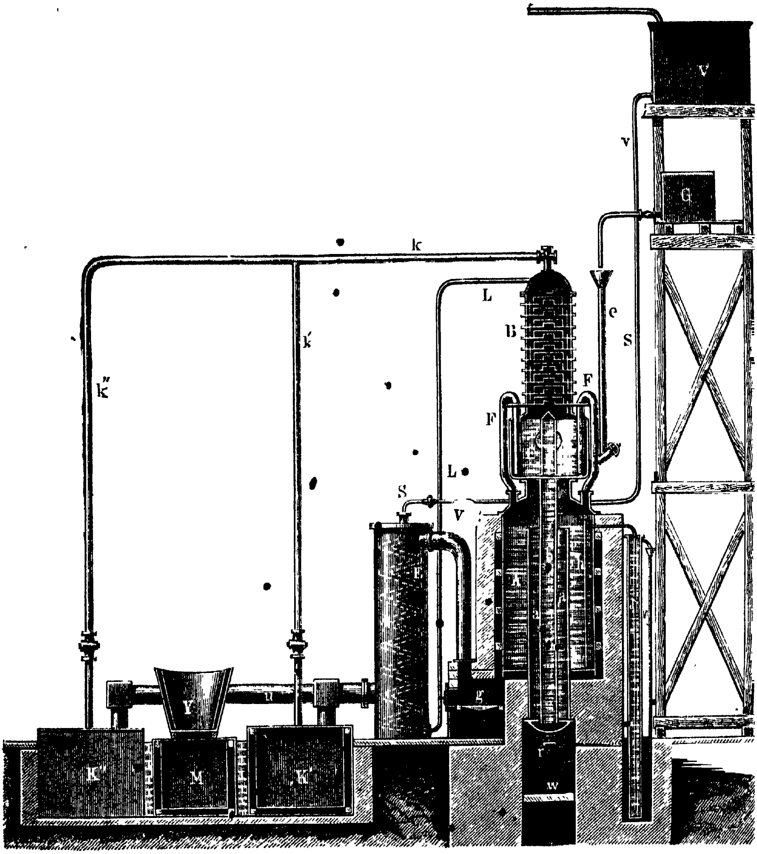


FIG. 307.

heating of the gas-liquor, which passes at S into a coil or set of pipes, in order to be conveyed through L into the column. From E the uncondensed gases pass through *v* into a fireplace *g*, where the offensive gases are consumed. The ammonium sulphate separated in K′ and K″ is put into the drainer Y, provided with a perforated false bottom; the mother-liquors collect in M.

The coal used averages 1 cwt. for each ton of gas-liquor passed through the apparatus; the lime, 15 or 20 per cent. of the ammonium sulphate produced. Two men can attend to an apparatus capable of distilling 10 tons per diem. Such an apparatus, without the lime-vessel, is 10 ft. high and 5 ft. wide; the column and lime-vessel add another 8 ft.

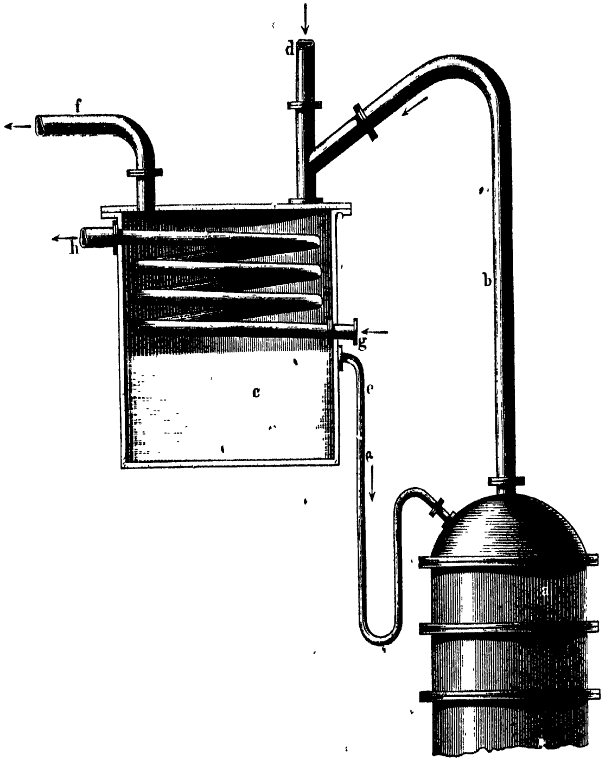


FIG. 308.

Some minor improvements of Grüneberg's apparatus are contained in the Ger. Ps. 15446 and 18852.

Practical experiences with Grüneberg's ammonia apparatus have been described by Kunath and Blum (*Fischer's Jahresber. d. chem. Techn.*, for 1884, p. 351).

The author owes the following further statements to the kindness of Dr Grüneberg. The two boilers A and C were later on made in one piece, of cylindrical form. The lime is introduced as sifted milk-of-lime by a membrane-pump. The milk-of-lime reservoir is an oblong iron tank with a vertical division, consisting of a fine sieve. The crude gas-liquor is now gradually heated in the following way, as shown in Fig. 308.

a is the top of the column, *b* the gas-pipe, *c* the liquor-heater; *d*, inlet for cold gas-liquor; *e*, overflow of the same and conduit into the column; *f*, outlet-pipe for the cooled gas. When heating the liquor in this way, the acid employed in the saturation must be of sp. gr. = 142° Tw. If weaker acid (106°) is to be employed, the heating of the liquor must be produced by the waste heat of the gases from the saturator, in order to have a sufficient evaporation in the same. If the object is making concentrated gas-liquor, the gases must be cooled as much as possible, and for this purpose there is on the upper part of the vessel *c* a worm, *g h*, through which cold water is constantly running.

A complete apparatus for sulphate of ammonia with lead saturator, liquor-heater, etc., for 10 tons gas-liquor costs 3500 marks (=£175). There were then more than fifty of these stills at work.

Apparatus of Grüneberg and Blum.

While the older Grüneberg stills are adapted to direct firing, a modification has been patented by Grüneberg and Blum (Ger. P. 33320), which seems preferable in all cases where there is steam at disposal. Fig. 309 shows the apparatus as adapted to the manufacture of sulphate of ammonia. In the column *a* the volatile NH_3 is expelled by steam, in B the fixed NH_3 by milk-of-lime, which is completed in C by open steam. In the saturator D the NH_3 is absorbed in sulphuric acid. The gas-liquor descends from *a* into B and C, where it is well divided by the steps, and is intimately mixed with steam, and completely deprived of NH_3; the spent liquor issues at *r*. The milk-of-lime is pumped by the hand-pump H at intervals of ten minutes into B. The tubular heater E, heated by boiler-steam, prepares the gas-liquor before entering the column. The ammonia vapours pass through *p* into the saturator D, made of wood lined with lead, and filled with sulphuric acid, about 1·4 to 1·45 sp. gr. The inverted lead bell *g* compels the vapours to bubble through the acid. The unabsorbed gases pass through *l* into *m*, where mechanically carried-away particles of liquid are retained. The residual gases are treated in the usual manner.

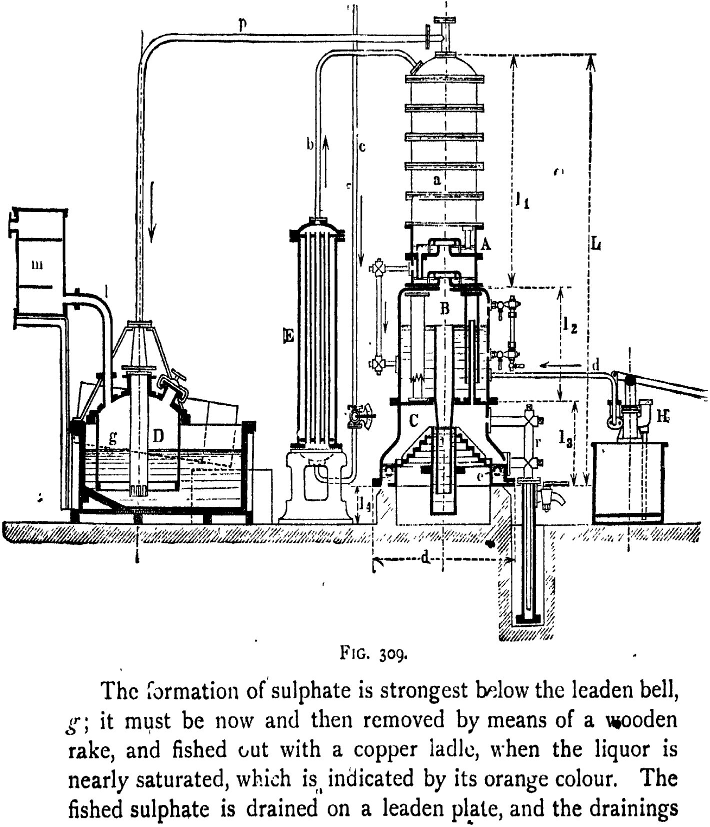


FIG. 309.

The formation of sulphate is strongest below the leaden bell, *g*; it must be now and then removed by means of a wooden rake, and fished out with a copper ladle, when the liquor is nearly saturated, which is indicated by its orange colour. The fished sulphate is drained on a leaden plate, and the drainings are run back into the saturator; the sulphate is then dried in a lead-lined stove or in special machines.

If the apparatus is properly working, the steam-gauge and water-gauges must be steady, the water must run off quietly, and the acid in the saturator must well up with a gentle movement. The carbonate of ammonia must by all means be driven out in the heater, since, if it gets into the lime-vessel, carbonate of lime is formed, which obstructs the apparatus. A tap at the bottom of the cellular heater admits of taking samples, which are tested with chloride-of-calcium solution. If this produces a precipitate of calcium carbonate, more steam must be admitted,

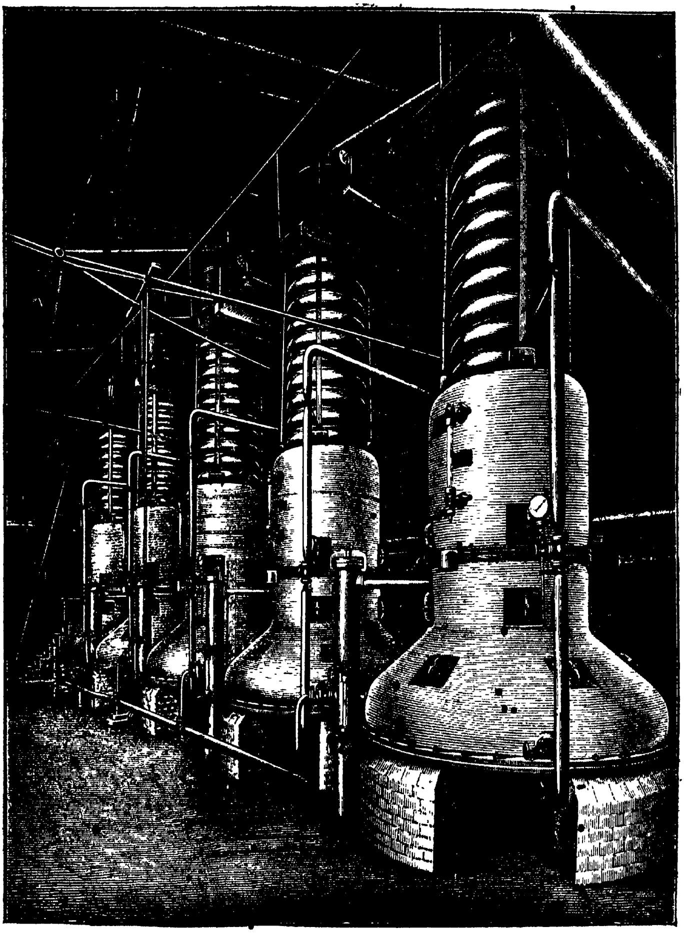


FIG. 310.

to complete the driving off of the ammonium carbonate. The waste liquor should not contain more than 5 parts NH_3 in 100,000. The gas-liquor must be first well purified from tarry matters, which clog up the overflow-pipes of the column. Obstructions by carbonate of lime occur mostly in the small tubes within the lime-boiler; if this happens, the apparatus must be stopped, the manholes opened, and the pipes taken out to be cleaned.

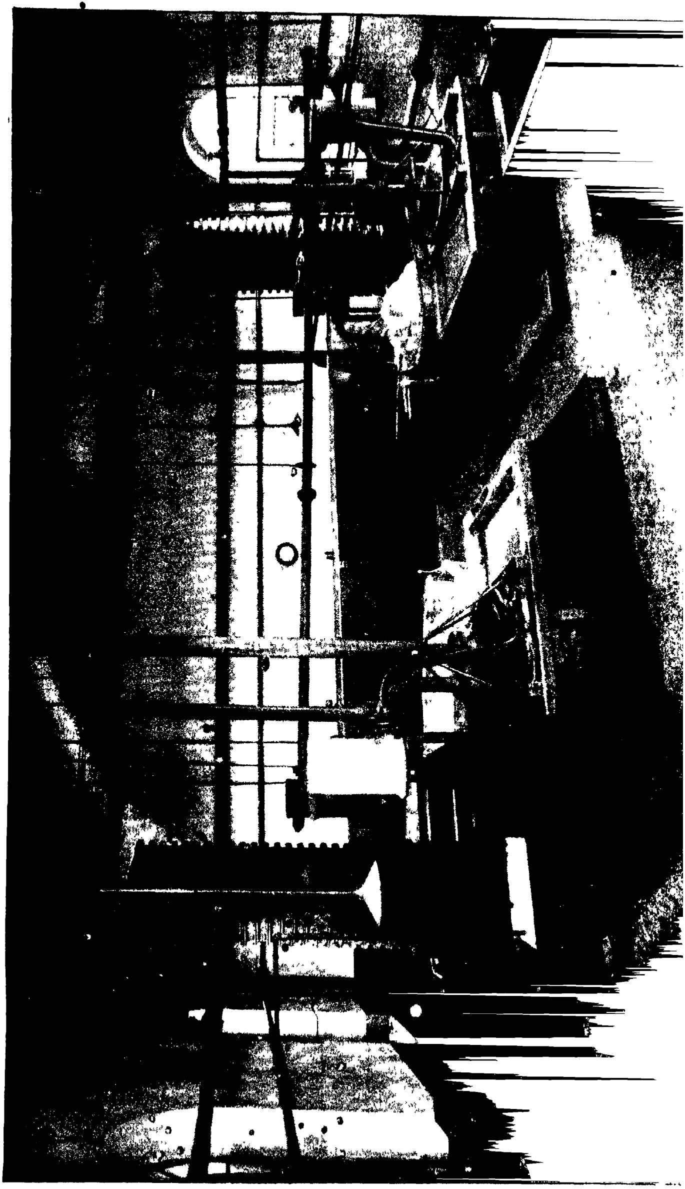
Fig. 310 shows five Grüneberg-Blum apparatus as erected at Messrs Kunheim & Co., near Berlin, working-up together 150 tons gas-liquor in twenty-four hours.

These ammonia-stills are made in six different sizes, to distil from 1300 to 6600 gall. of gas-liquor per twenty-four hours. According to trustworthy evidence, they answer very well indeed: the ammonia left in the liquors is, on the average, not above 0·05 per cent.; there is but a small consumption of steam, very little labour, no nuisance, and no trouble.

In *J. Gasbeleucht.*, 1901, p. 895, Blum describes an automatically acting pump for the milk-of-lime with automatic action.

Watson Smith (*Industries*, 1886, p. 242) gives the following calculation for distilling in a Grüneberg-Blum still the gas-liquor obtained in carbonizing 35,000 tons of coal, viz., about 35,000 tons of liquor at 5½° Tw.:—

	Tons.	Price. s.	Price. d.	£	s.	d.
Sulphuric acid, 142° Tw.	389	40	0	778	0	0
Lime	71	12	6	44	7	6
Labour—4 men 50 weeks, at	...	25	0	250	0	0
Coal	175	8	0	70	0	0
Casks and packing	...	...		155	12	0
Sundries, repairs, etc.	...	...		116	14	0
Depreciation of plant, £300, buildings £150: total £450—at	...	10 p.c.		45	0	0
Interest on plant and buildings £450, land £100: total £550—at	...	5 p.c.		27	10	0
Gas-liquor 5¼° Tw.	3500	12	0	2100	0	0
				£3587	3	6
Produce, sulphate of ammonia	389	£11		£4279	0	0
Deduct cost of manufacture	...			3587	3	6
				£691	16	6



C. T. & A.

Fig. 311 shows the apparatus for the manufacture of ammonium sulphate as fixed at the Constantia pit, in Westphalia.

Feldmann's Apparatus.

Dr A. Feldmann, of Bremen, has constructed an ammonia-still (Ger. P. 21708; B. P. 3643, of 1882) which is very much recommended, and of which very many are at work in different countries. It is a steam-still, and is adapted for making sulphate, liquor ammoniæ, or concentrated gas-liquor. Its principle is that of a continuously acting column where not merely the volatile ammonia but also the fixed ammonia, set free by lime, is driven off. Otherwise the principle of 'the dephlegmation-column' is the same as that adopted in the Coffey still, the Grüneberg still, and many others.

Considering its great capabilities, the apparatus requires but little room for setting up. An apparatus to distil from 8 to 10 tons of ammoniacal liquor in twenty-four hours occupies a space of 17 ft. by 13 ft. by 10 ft.

The apparatus (Fig. 312) consists of the column A, decomposing-tank B, and column C. The ammoniacal liquor flows from the feed-tank *a* into the supply-tank *b*, the object of which is to obtain a regular flow into the column through pipe *c* into the tubular boiler J, and thence through *d* into the top chamber of column A. From here it passes through the overflow-pipes *a* from chamber to chamber, in each of which it is boiled up by the steam which fills the stills, and is delivered free from all volatile ammoniacal compounds, through a long overflow-pipe, *a'*, almost at the bottom of the decomposing-tank B. Into this tank milk-of-lime is introduced through the pump G, and the inflowing gas-liquor is constantly mixed by a steam agitator. The inlet of steam is so regulated that the decomposed gas-liquor must run out at the top of tank B; and by the working of a sieve, introduced to break the ebullition, it passes purified and freed of surplus lime through siphon *e* into column C. In the separate chambers of this column, the ammonia formed is driven out, the spent liquor collects in the part D, and flows constantly through the tap *f*. The steam required for distilling is admitted through pipe *g* into column C; traversing the fluid in each separate chamber, it passes through pipe *h* and tank B into column A. It then rises through all the chambers in A, and leaves, charged with accumulated ammonia, by the exit-pipe *i*. Finally it arrives under the leaden bell F, which is partly submerged in sulphuric acid, contained in the lead-lined cistern E. The ammonia combines with the sulphuric acid; the gases which have not been absorbed, such as carbon dioxide, hydrogen sulphide, etc., mixed with steam under the leaden bell, are conducted through the exit-pipe *k* into the cylinder J. The action of this cylinder is exactly similar to that of the economizer in Grüneberg's apparatus, so that we need not repeat its description in this place; nor need we go into the treatment of the gases. The essential difference between Feldmann's and Grüneberg's apparatus consists in this: that the former, after driving off the volatile ammonia, saturates

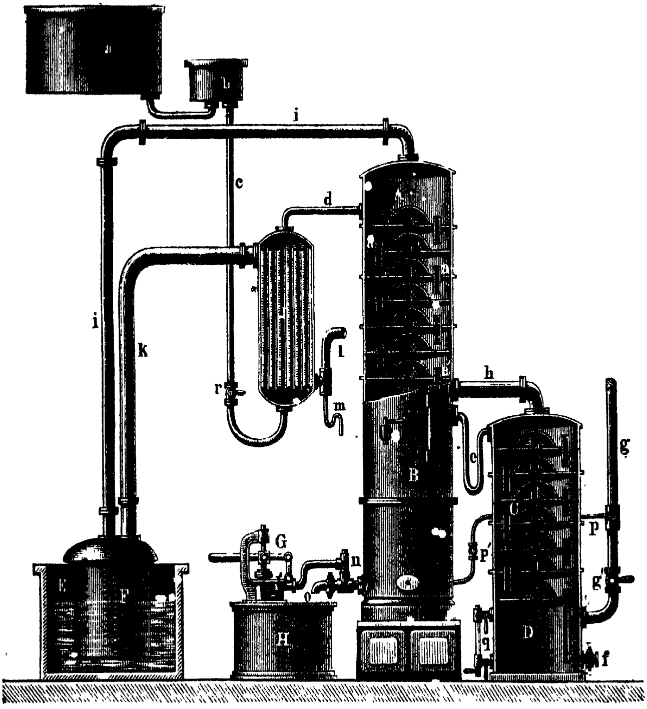


FIG. 312.

the liquor with lime, and sends it in a *clear* state through a second column.

The usual sizes of the apparatus are for distilling 5, 10, or 15 tons of ammoniacal liquor per day; but it can be made to distil very much larger quantities. At Silvertown there is a still for 80 tons, and at Runcorn one for 200 tons liquor per day.

This apparatus (according to reliable information) easily drives off the ammonia to such an extent that the distillation test of the residues does not show more than 3 to 5 parts NH_3 in 100,000 parts of liquor; and the liberation of the NH_3 can be made practically absolute.

A very striking example of the difference between the old two-boiler system with direct firing and the rational new apparatus is afforded by a return made by the Bielefeld Corporation Gas-works. Formerly they worked only 2½ tons liquor in a two-boiler apparatus with direct firing. The result of a hundred days' working was 466 cwt. of damp, greenish sulphate, with barely 20 per cent. nitrogen. The wages per cwt. of sulphate amounted to 0·91 mark, the consumption of coke to 2·87 scheffel = 0·86 mark. After putting up a Feldmann still, the daily consumption of gas-liquor was raised to 7½ to 8 tons; the yield of sulphate upon the coal treated in the retort was 0·9 per cent. The output of sixty-three days' working was 684 cwt. of nearly white sulphate, with 20·68 per cent. nitrogen. The expenses were as follows, per cwt. of sulphate:—

	Mark.
82·6 lb. sulphuric acid, 168° Tw., at 4 mark per cwt.	3·20
1·5 scheffel coke, at 0·30	0·45
Wages (at 4·24 mark per diem)	0·40
Lime	0·15
Sundries (lighting, shovels, etc.)	0·15
Amortization and interest	1·00
	5·35

Feldmann claims that his apparatus obviates the difficulty of obstructing the column by a precipitation of lime and lime-salts in a much simpler way than is done by P. Mallet (see p. 1446); and that the employment of a column for expelling the fixed ammonia permits not merely doing this in the most perfect possible manner, but also by a minimum of steam.

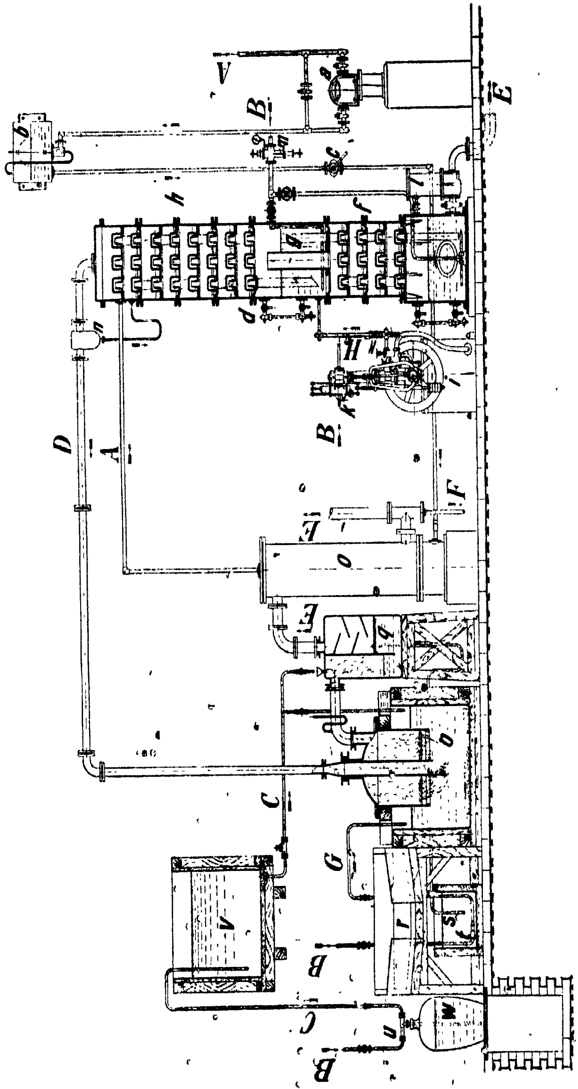


FIG. 313.

This is most important when utilizing the gas-liquor for manufacturing sal-ammoniac, where there should be as little subsequent evaporation as possible; but it is also very useful in making sulphate of ammonia, because it greatly facilitates the dealing with the sulphuretted hydrogen.

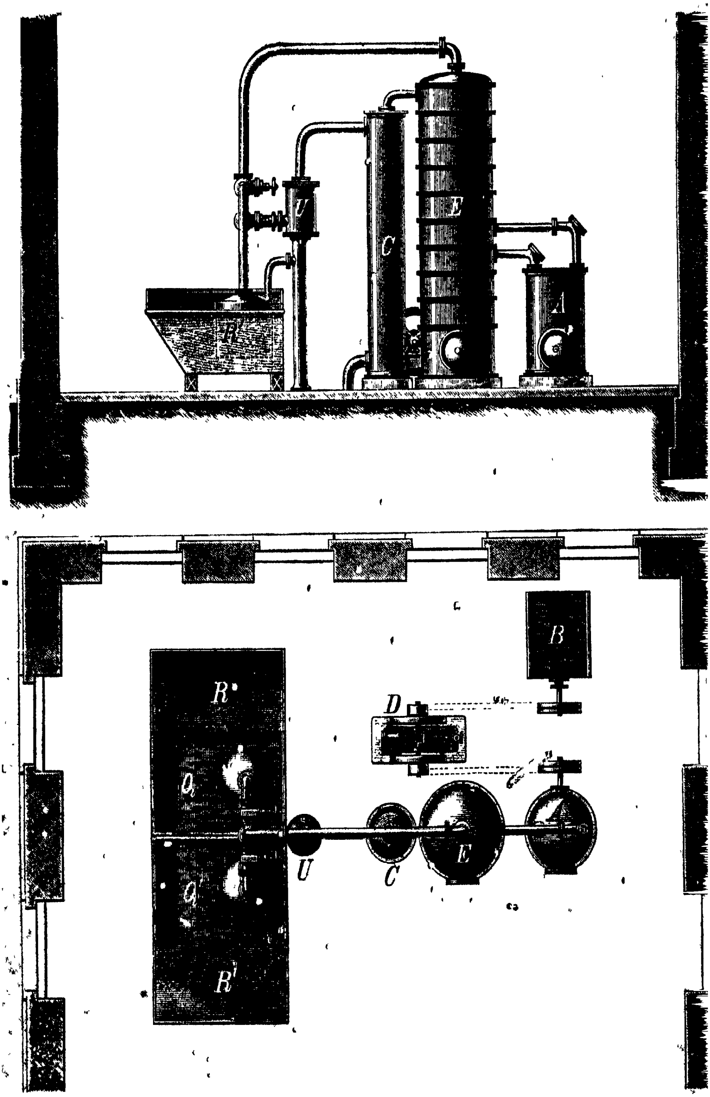
A more recent German patent of Feldmann's (No. 71909) describes a lime-boiler and a number of distilling cells ranged all round it, through which the gas-liquor runs from one to the other, and ultimately into the lime-boiler. A further patent of his (Ger. P. 134976) describes some improvements in the saturator bell.

Apparatus of Julius Pintsch.

Fig. 313 shows the apparatus as constructed by the firm Julius Pintsch Aktien-Gesellschaft, of Berlin. The gas-liquor enters through pipe A, flows through the measuring-apparatus *a*, then through the floating-bell regulator *b*, which secures a constant height and consequently uniform supply of the liquor, thence through tap *c* into the preheater *o*, where it is heated up by the waste gases from the saturator *p*, and then through A into the top chamber of the column-still *h*. Descending in this, it gets into chamber *g*, where it is mixed with milk-of-lime, supplied by pump *k*, then into the lower column *f*, and leaves this through the automatically regulated outlet *l* and the escape-pipe E. The steam enters at the bottom of the column and travels in the opposite direction to the liquor, leaving the column at D and carrying all the gases into the sulphuric-acid saturator *p*. The waste gases are deprived of the last ammonia in the box *g* and from here get into the above-mentioned preheater *o*, where their heat is utilized for warming up crude liquor. The gases escaping from here go away into the chimney, or else through an oxide-of-iron purifier for retaining the H_2S. V is a tank for sulphuric acid, into which it is forced from the store-tank *w* by the steam-jet *u*. This firm gives in Lunge and Koehler's *Steinkohlenteer und Ammoniak*, 5th edition, 1912, ii., pp. 379 *et seq.*, detailed calculations concerning the financial results obtained with their apparatus.

Apparatus of Heinrich Hirzel.

Heinrich Hirzel's column (Ger. P. 64367) is built on the same principle as that which he has constructed for liquor ammoniæ (pp. 1374 *et seq.*). In Figs. 314 and 315, D is a steam-



FIGS. 314 and 315.

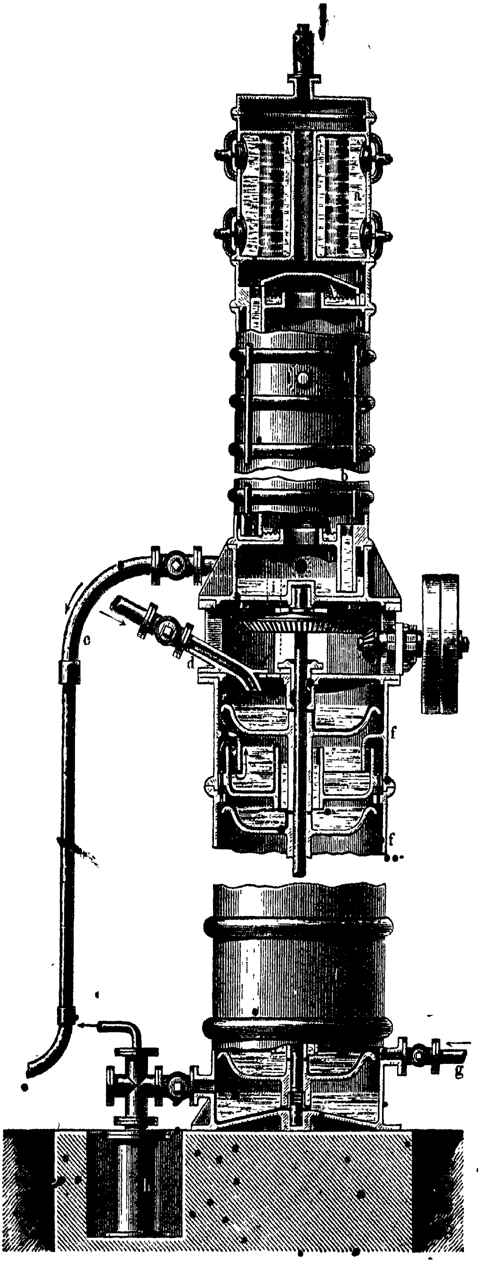


FIG. 316.

pump, by which the gas-liquor is forced into the heater C, and from this into the upper part of the column E. In this the carbonate and hydrate are expelled; about the middle of the column the liquor issues into the agitating-vessel A, where it is supplied with milk-of-lime from vessel B, and then returns into the column. The gas enters one of the two lead saturators Q or Q′, according to the position of the valves, underneath the lead bells. The gases not taken up by the acid pass through the catch-all U′ to retain any acid carried away, then through the heater C, where they give up part of their heat to the gas-liquor traversing the heater in a coil of piping, and at last issue into the atmosphere. The sulphate is fished from Q and Q′, and drained on the slanting plates R and R′. These apparatus are built to work from 1 to 40 tons gas-liquor in twenty-four hours.

Improvements of Hirzel's apparatus are described in his Ger. Ps. 88953 and 91717.

P. Mallet's Apparatus (1884).

P. Mallet (*cf.* 1375 and 1400) has set himself the special task of making an "inobstructible column" for distilling ammoniacal liquor in contact with lime, without having to clarify it by repose (as is necessary especially for liquors produced in the treatment of sewage), or without having to relegate the lime treatment to another vessel. His apparatus is shown in Fig. 316. An ordinary column, *b, b*, surmounted by an "analyzer," *a*, serves to expel the volatile ammonia. From here the liquor runs off by *c* into an apparatus (Fig. 317) intended for mixing with lime. This consists of a closed hopper, *k*, which is charged with a sufficient quantity of quicklime to serve for several hours, and of an endless screw, *l*, which conveys this lime to the mixer *m*; here it is mixed with the liquor entering at *c*, which slakes the lime, and carries it in a state of suspension through the pipe *d* into the inobstructible column. The valve *n* serves for removing from time to time unslaked pieces, stones, etc. The mixture of lime and liquor now descends in the lower column *f* (Fig. 316) from plate to plate; the revolving shaft in the centre of this column, by means of scrapers fixed to it in each of the chambers of the column, keeps the lime suspended in the liquor and prevents the formation of any crusts on the plates. The spent liquor is cast out by the mechanical purifier *h*; for very dirty lime a sludge-box must be provided, from which the deposit is taken out from time to time.

A special advantage claimed for this apparatus is that it works with quicklime and utilizes the heat of slaking, at the same time dispensing with the necessity of sifting the milk-of-lime; but it does not appear that this is a feature essential to the "colonne inobstruable," whose principal speciality, the revolving shaft, is evidently not without its drawbacks. Many manufacturers will prefer a simpler apparatus, dispensing with machinery.

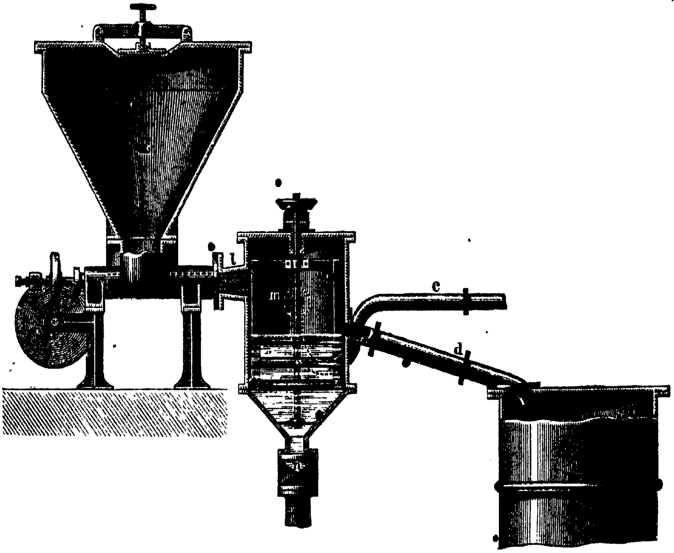


FIG. 317.

Various Forms of Ammonia-Stills.

A revolving column has been patented by W. T. Walker (B. P. 16806 of 1887).

Dempster (B. P. 22602, of 1893) runs the previously heated liquor into a vessel, at the bottom of which steam is injected; at the top the liquid, carried along by steam, strikes against a splash-plate, which converts it into a spray. The exhausted liquor travels by an overflow into a second vessel, where it meets with lime.

Spence and Gilchrist (B. P. 7845, of 1893) describe special contrivances for mixing the lime with the liquid after distilling off the free ammonia.

Eckelt (*Chem. Ind.*, 1893, p. 451) describes a special overflow-pipe. Bowen (B. P. 18356, of 1889) passes heated air or oxygen through the boiling liquid, and conducts the mixture of gases and vapours given off into receivers charged with ferrous sulphate, which is thereby oxidized, the NH_3 precipitating ferric hydrate, and being converted into sulphate, and the H_2S being retained at the same time.

Outon (*Gas World*, 1905, p. 353) describes a sulphate plant, specially adapted for smaller works, but not presenting any specially new features. The same must be said of a paper by Keillor (*J. Gas Lighting*, 1903, p. 361), which is, however, interesting to gas managers by its discussion of the financial side of sulphate-making.

Francke (Ger. P. 165309) makes the steam, injected into the still, strike against blades, fixed to a movable spindle, or to the bell itself, which in this case must be movable. These blades are shaped in such manner that the liquid, rising in the still on striking against them, favours the rotation of the bell. This arrangement causes a much better mixture of the lime with the liquid than the mere action of a steam-jet.

The same inventor later on (Ger. P. 169444) arranges the bells of a distilling-column in such manner that they can be raised or lowered from without, in order to regulate the depth to which they dip into the liquid and to facilitate the cleaning out of the column.

Adriaanse (Ger. P. 185196; Fr. P. 355971) provides the lower bells attached to the agitator, with stirring-blades reaching nearly down to the bottom of the shelves, so that they prevent a deposition of lime during the work and admit of cleaning out the still without opening its sides.

G. Wilton (B. P. 24832, of 1901) arranges on the trays of the distilling-column narrow, elongated steam openings, provided with hoods dipping into the liquid, and mud holes in the walls of the chambers opposite the end of these openings.

T. and G. Wilton (B. P. 28251, of 1902) describe a continuously working still, especially for use in small works, consisting of superposed cylinders with movable caps in which are fitted the various connections. A furnace heats the lower chambers, either by steam or by a direct fire, and the hot gases heat the upper chambers.

The ammonia-stills of Jacob Schaefer, at Höchst, have been introduced in many places, both in Germany and abroad. They are, like many others, a combination of a lower part, where the non-volatile ammonium salts are decomposed by means of lime, with a superposed column, where the volatile salts are expelled from the liquor by the steam produced below, with a special arrangement for preheating the liquor before it enters the column. According to a report received from Mr Ernest Heuss, of Nied, near Frankfort, the Schaefer stills do excellent work and are very easy to deal with.

The Société J. Jean & Cie. (Fr. P. 372171) promote the expulsion of ammonia by a finely divided current of air, employing 1400 vols. air for 1 vol. gas-liquor and a velocity of the air current of 100 ft. per second. The mixture of air and vapours is hurled against large surfaces, in order to precipitate the foggy particles.

Koppers (B. P. 2399, of 1908; Ger. P. 191722) describes an ammonia-still, in which the liquor flows through parallel channels, in the various chambers, alternately from the centre outwards, or from the outside towards the centre.

Dill (Ger. P. 200592) patents a special shape of ammonia-stills, built up from boxes in a zigzag line, with the usual fittings of continuously working ammonia-stills, adapted to being readily exchanged for purification.

Scott (B. Ps. 3987, of 1900, and 11802, of 1901) describes various modifications of ammonia plant. So do Abendroth (U.S. Ps. 712891, of 1902, and 771031, of 1904); Osius (U.S. P. 710221, of 1902); Moore (U.S. P. 740678); Erlenbach (Ger. P. 203309).

Ballantyne (*J. Gasbeleucht.*, 1903, p. 755) describes a "new continuous vacuum process," the plant for which is similar to ordinary ammonia plant, but is kept under a vacuum of 13 to 15 in. mercury in the still and 22 to 27 in. mercury in the saturator, The main object is a saving of fuel. (See below, under the heading "Saturators.")

G. E. Davis (B. P. 26996, of 1903) constructs ammonia-stills with serrated caps, fixed to the plates forming the tops of the chambers, so that the serrations hang free in the liquid, allowing a small rake to be inserted underneath the caps for removal of the deposit.

Holmes and Howell (B. P. 24913, 1907) employ an ammonia-still in which an intermediate liming-chamber is interposed between the upper and lower chambers, and they facilitate the removal of sludge by making the floor of the liming-chamber dished or conical, so that the sludge tends to settle towards the outlet leading to the sludge-valve. Injectors may be placed at intervals round the chamber, so as to produce a current for preventing any settlement of the sludge near the periphery.

Further Apparatus for the Manufacture of Ammonium Sulphate from Ammoniacal Liquor.

Barnick (*Chem. Apparatur*, 1915, p. 61).

W. H. Wright (U.S. P. 1114843).

Davis (B. P. 164349, of 1889); Ellis (B. P. 13003, of 1889); Holgate (B. P. 3684, of 1890); Mather (B. P. 17824, of 1892); Carr (B. P. 16978, of 1898).

Carl Francke, Bremen (Lunge and Koehler, *Steinkohlenteer und Ammoniak*, 1912, ii., p. 370).

Heinrich Hirzel, Leipzig-Plagwitz (*ibid.*, p. 373).

Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft (*ibid.*, 375).

Carl Hill, Recklinghausen (*ibid.*, p. 376).

Chemical Engineering and Wilton's Patent Furnace Co., London (*ibid.*, p. 378).

Obtaining Ammonium Sulphate free from Cyanides.

Grossmann (B. P. 20387, of 1905), in order to obtain ammonium sulphate free from cyanides, *without producing offensive waste liquors*, distils the gas-liquor first without lime, then boils down the remaining liquor, and adds sulphuric acid, to decompose the cyanide and sulphocyanide. The liquor now remaining behind is used over again for the absorption of ammonia. He fully discusses his process in *J. Soc. Chem. Ind.*, 1906, p. 411, whereof we give an abstract here. The principal motive for his invention was, that, even if it were possible to remove the cyanogen compounds economically, there would still be left sufficient tarry compounds and compounds of the nature of phenols, to render the final effluent noxious; and there is no method of removing these organic compounds. His own process (which at that time evidently had not yet been carried out in practical work) follows in the main like the present mode of manufacture, and branches off at a convenient point.

In the first place, the ammonia liquor is distilled by means of steam in the same stills as those used at present, but with this difference, that no lime or other alkaline substance is added. The resulting liquor contains all the fixed salts of ammonia, besides tar-oils and phenols and salts of sodium. When carbonizing 200 tons of coal per day, the total quantity of liquor leaving the still is about 10,000 gall. per day, of which 3000 gall. of water are freshly formed every twenty-four hours. The remaining 700 gall. can, after cooling, be used again in the scrubbers for absorbing a further quantity of ammonia and ammonia compounds, and we shall only have to dispose of the 3000 gall. in such manner as to avoid a nuisance.

The figures given here are actual results obtained frequently in gas-works and sometimes in coke-works. In the latter, [redacted] the quantity of water formed every day often exceeds the figures given here, as the coal used may contain 10 per cent. and more of moisture. It would be to the coke manufacturer's advantage to reduce this quantity to its lowest point by using the coal as dry as is practicable.

That portion of the liquor which goes back to the scrubbers will gradually become richer in dissolved fixed ammonia and other compounds. But it will reach its limit when that portion which is withdrawn every twenty-four hours for further treatment becomes of such strength that it contains as much in fixed compounds as will be equal to the total quantity of these compounds which the apparatus will produce in every twenty-four hours.

The quantity to be dealt with in the process would mainly depend on the quantity of moisture contained in the coal. This quantity would vary from 3000 gall. in good, dry coal to about 9000 gall. in coal containing 15 per cent. of water and 5 per cent. of other water-forming constituents.

Whatever be the quantity of liquor thus obtained, it must be evaporated to a small bulk to become amenable to further treatment. It may be generally taken that the ultimate bulk after evaporation will correspond to about 1¼ gall. for every ton of coal carbonized. It will then form a strong solution of ammonium chloride and thiosulphate, besides containing some thiocyanate, sodium chloride, and possibly some ferrocyanide. Ammonium chloride can at this stage be removed to a considerable extent by cooling and crystallizing; and as some of the samples examined contained up to 20 per cent. of the total ammonia going to the stills as ammonium chloride, the recovery of the ammonium chloride as such should yield considerable profit.

The remaining mother-liquor will now contain chiefly thiosulphate, chloride, and thiocyanate. This liquor is placed in a still and neutralized with weak sulphuric acid so as to decompose the thiosulphate. After agitation, such a quantity or more of sulphuric acid of about 120° Tw. is added as would form ammonium hydrogen sulphate with the ammonia contained as thiocyanate. On heating to about 100° C. or less and agitating, the thiocyanate becomes partly decomposed, and partly distils over as such. On passing the gases through limestone, a pure solution of calcium thiocyanate is obtained; hydrochloric acid is not liberated if the temperature and other conditions are followed out according to the above. After passing the calcium-carbonate absorber, the gases are taken through a mixture of an iron salt with alkali, or through oxide-of-iron purifiers; and in either case sulphuretted hydrogen and cyanogen compounds other than thiocyanate are thus removed.

The liquor from this still, which contains ammonium sulphate, chloride, and free sulphuric acid, but no thiocyanate, may be used for diluting the sulphuric acid which is employed in the saturator. It will, however, in existing installations probably be better to use a separate saturating-box built of stone for this liquor, and take part of the ammonia from the main into it, so as to avoid any chance of the lead in the old saturator being attacked by any hydrochloric acid which may be set free. In new installations, the ordinary saturator would serve the purpose if made of material which will resist hydrochloric acid, always provided that it was found that the liquor coming from the sulphocyanide still attacked lead.

One great advantage of the method is that it enables us to recover the ferrocyanide as well as the thiocyanate without interfering with the plant as it is in use at present. It is well known that many processes have been designed to remove the cyanides and ferrocyanides from the gaseous products of coal distillation by passing them through alkaline emulsions of ferrous oxide. All these processes require special washing-apparatus; and in the case of gases from coke-ovens, it is said that the results obtained have been unsatisfactory. Two ways of recovering cyanides and ferrocyanides are open in Grossmann's method. Where the quantity of these compounds is large, they may be removed as insoluble ferrocyanides or zinc ferrocyanides by adding ferrous or zinc sulphate in exact proportion (to be previously ascertained by test) to the evaporated liquor, and neutralizing carefully with sulphuric acid. After filtering, the liquor may go to the still and be treated with a further quantity of sulphuric acid in order to eliminate the sulphocyanogen. But where the quantity of ferrocyanide is not excessive, there is no need of any treatment of this kind, as the ferrocyanides will become decomposed in the still in presence of an excess of sulphuric acid, evolving hydrocyanic acid, which will be absorbed in the alkaline or in the iron oxide purifier, and thus allow of the recovery of these compounds in the shape of ferrocyanide.

Grossmann contends that the cost of his process will in no case exceed in cost of working that of the present method. There is a saving in not using lime, which amounts to 3s. per ton of ammonium sulphate, and a saving in the quantity of steam used; and the amount of labour should be the same as before. There should be a gain in the yield of ammonium sulphate equal to about 4s. per ton, as no ammonia left in the waste liquors from the stills is eliminated from the system. There is a gain through the recovery of thiocyanate and ferrocyanide, which, taking them at only 1d. per pound, would amount to from 4s. to 20s. and more per ton of ammonium sulphate; and the extra profit on ammonium chloride may be put down at from 9s. to 13s. and more. Against this probable saving of from 20s. to

40s., we have to allow for the cost of evaporation, the cooling of the liquors, and the amortization and depreciation of the extra plant required. The cost of the first item will greatly depend upon local circumstances. Where the amount of water in coal is normal, there should be sufficient waste-heat in coke-oven works to render this operation free from being a charge on the process. In gas-works, where there is no waste heat, the charge should not amount to more than 5s. per ton of sulphate of ammonia, as there is always in these works sufficient coke-breeze to spare, which has only a low commercial value, and in some cases almost none. Even where the amount of liquors produced is excessive, it will, in many cases, be found that there will be sufficient waste coal and coke of unmarketable quality which can be used for evaporating purposes. The cooling of the liquor also depends on local circumstances; but, even under the most unfavourable conditions, the charge for it would be small. The depreciation of the plant could only take place in the evaporating apparatus, which is not expensive. The process has not been designed with a view to effecting a saving in manufacture, but in order to improve it in a sanitary respect. If it will accomplish that without extra charge to the manufacturer, it will have done all that can be reasonably expected.

A new process for obtaining ferrocyanide, by the same inventor, will be mentioned *infra*, Chapter XVII.

Treatment of Ammoniacal Liquor in the Cold State for removing Hydrogen Sulphide and Carbon Dioxide.

We have already mentioned *supra*, pp. 1361 *et seq.*, some of the processes belonging to this class in connection with the manufacture of pure liquor ammoniæ. Here we speak of processes connected with the manufacture of sulphate.

These processes are not much practised. Some have proposed *ferric hydrate*, which acts as follows:

$$Fe_2(OH)_6 + 3(NH_4)_2S = 2FeS + S + 6NH_3 + 6H_2O.$$

Thus ferrous sulphide, sulphur, and free ammonia are produced; the two former remain behind. The residue can be revivified till it is rich enough in sulphur to be utilized for the manufacture of sulphuric acid, or for the sulphur to be recovered by distillation. For the latter purpose Gerlach (Ger. P. 229) employs superheated steam, as offering great advantages.

Sometimes *soluble salts of iron or manganese* are added to the gas-liquor before distillation, in order to remove the sulphide. The precipitate might be filter-pressed, and the residue revivified as just mentioned. But this process, like the former, is not very simple and cheap.

A special process for removing sulphuretted hydrogen from gas-liquor is that of Kunheim & Co. (Ger. P. 26422), which aims at fully utilizing the sulphur. The crude gas-liquor is treated in the *cold* state with a strong current of atmospheric air, divided into many jets. This dissociates the ammonium sulphide into ammonia and hydrogen sulphide, the latter being carried away by the air. The gaseous mixture is conducted through finely divided ferric hydroxide, and the hydrogen sulphide is here absorbed. For this purpose native hydrated oxide of iron, or an artificial precipitate, or even other hydrated metallic oxides may be employed. The ferric hydroxide is kept suspended in a dilute solution of alkaline earths. Fig. 318 illustrates the process. The gas-liquor is introduced by means of a force-pipe through the pipe *p* into the boiler K

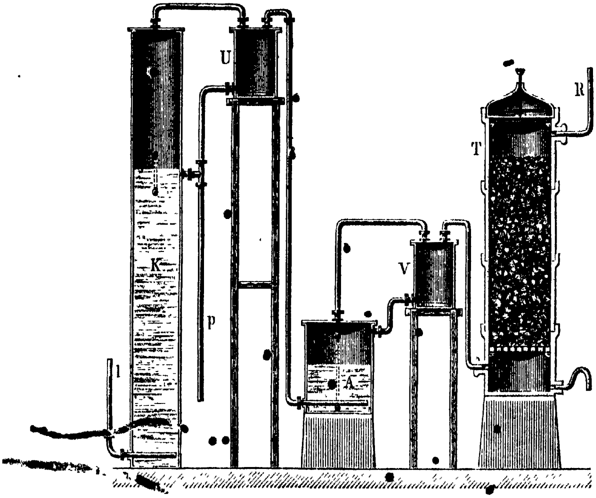


Fig. 318.

into which a strong current of air is forced by means of a blast or injector through *l*. The gas-liquor mechanically carried away is retained in the safety-vessel U, and is continually returned into K. The mixture of air, hydrogen sulphide, and a little ammonia is conducted by a perforated pipe into the vessel A, half-filled with a mixture of ferric hydrate and lime-water. Here the H_2S is absorbed, but the FeS formed is at once changed by the air into free sulphur and regenerated ferric hydrate. The excess of air and some ammonia first pass through the safety-vessel V, where so much of the pasty mixture as has been mechanically carried away is retained and flows back into A. From here the gases pass through the stoneware coke-scrubber T, where the ammonia is absorbed by a shower of sulphuric acid. The air escapes through R into the atmosphere, or first into a chimney. The gas-liquor remaining in K, and now freed from sulphide, is in the usual way caustified by lime and distilled. The here-described process of absorbing hydrogen sulphide by a mixture of ferric hydroxide with lime, with a simultaneous introduction of air for reconverting the ferrous sulphide formed into free sulphur and ferric hydroxide, may also be employed for dealing with hydrogen sulphide from any other source. [It is only right to state that the absorption of sulphuretted hydrogen by a mixture of ferric or manganic hydroxide and lime, suspended in water, was described by myself as early as 1866, in the B. P. 1108; and Weldon, in his patent of 18th August 1871, and again in 1876, added to this the regeneration by air in the liquid state. The simultaneous passage of air, along with the H_2S, through the mixture of ferric hydroxide of lime was also tried by myself about that time, but nothing was published concerning it, as the experiments could not be followed out to a definite issue. *Cf.* also the *Alkali Inspectors' Reports* quoted lower down.]

A somewhat similar process is that of Holgate, of the Halifax gas-works. He submits the raw liquor to a moderate heat, produced by passing the waste gases from the sulphate of ammonia saturator into a box through which the gas-liquor is made to flow in a coil of 2-in. tubes. By this means most of the H_2S and CO_2 is driven off, whilst most of the NH_3 remains behind. A table given on p. 31 of the *Thirty-sixth Report of the Alkali Inspectors* shows that by this treatment only from 16·9 to 26·5 per cent. of the NH_3 is driven out, whilst 54·5 per cent. of the CO_2, and 84·6 per cent. of the H_2S is removed.

Wolfrum (Ger. P. 40215) produces a solution of basic ferric salts by suspending 1 part spent oxide of iron in 2 or 3 parts water, adding ½ to 1 part sulphuric acid or 1 or 2 parts hydrochloric acid, and dissolving in each 50 parts of this mixture 5 or 6 parts iron-ochre. This solution serves for disulphurizing fifty or sixty times its volume of raw gas-liquor. The precipitate produced contains about 30 per cent. sulphur soluble in carbon disulphide.

Fousset (Fr. P. 382269, of 1906; B. P. 253[illegible]1, of 1907) also employs for the working-up of ammoniacal liquors an apparatus working in the cold. The liquor, after adding fixed alkali, if necessary, is "atomized," and in this condition allowed to fall down a vertical drum, in which it meets an ascending current of air which carries the ammonia with it as gas. This air passes between zigzag partitions, on which it deposits any spray, and then impinges against a rotating fan which is kept supplied with dilute sulphuric acid.

Kestner (B. P. 1843, of 1906) proceeds in the same way. He atomizes the liquor by means of a Kestner centrifugal atomizer in a current of air, say, 180 vols. of air to 1 vol. of ammonia liquor containing 2 g. NH_3 per litre. It will be found that the liquor issuing from the apparatus does not contain more than 0·015 g. NH_3 per litre, so that 99·25 per cent. of the ammonia passes away with the air. In the case of 300 vols. air to 1 of liquor, only about 0·005 g. NH_3 remains after atomization. The air is then passed over sulphuric acid, which takes out all the NH_3, so that this process is practically a cold process for the recovery of NH_3 from ammonia liquors.

Similar processes have been patented by Feld (Ger. P. 188636) and Brandenburg (Ger. P. 189830).

Warth (*Chem. News*, xcii., p. 259) by agitating gas-liquor with gypsum recovers 80 per cent. of the ammonia in the state of sulphate, so that only one-fifth of the ammonia need be got by boiling and absorbing in sulphuric acid.

Apparatus specially intended for Working Sewage.[1]

A considerable number of these are described by C. Vincent in the *Encyclopédie Chimique*, 2nd section, tome x., part 4, pp. 14 *et seq.*; but most of them present nothing calling for special recommendation, as the older apparatus of Figuera, of Margueritte and Sourdeval, and others; or else they are only various forms of combinations of boilers with dephlegmating-columns and heat-economizers, not different in principle from those already described, as the apparatus of Lair, of Sintier, and Muhé, etc. That of Hennebutte and Vauréal has a very peculiar form, but the principle is still the same. We would refer for descriptions and diagrams of these apparatus to M. Vincent's book; also for that of Chevalet's apparatus for treating turbid sewage and "tout venant," that is, the whole contents of the sewers, including night-soil and all other solid refuse. We will, however, describe two other apparatus constructed for the same purpose.

P. Mallet's Apparatus for treating Thick Sewage

is shown in Fig. 319. It consists of a tubular heater, A; a tubular vapour "analyzer," B; a cast-iron column, C, 4 ft. 8 in. wide, serving as dephlegmator. This column, by means of a hollow stand, rests on the top of the agitating-column E. The latter has a diameter of 6 ft. 8 in., and contains a number of plates with central holes; a central shaft, made to revolve with toothed gear, carries a set of stirrers ranging over every one of these plates. The sludge-decanter F forms the bottom of the whole system. The sludge itself is discharged into trucks, W, whilst the clear, decanted, boiling part of the spent liquor passes on to the heater A, and afterwards, being completely cooled down, runs off through the tube *s*.

The fresh sewage matter is forced by means of a pump through the pipe *a* into the heater A, and passes through its tubes; on its way it gets heated by the spent liquor, circulating in the opposite direction, before issuing at *s*. The sewage then ascends through the 4-in. pipe *b* into the analyzer B, in which it is further heated by the vapours ascending from the rectifier C; it then passes out by the siphon-tube *c* into the column C

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[1] *Cf.* pp. 1154 *et seq.*

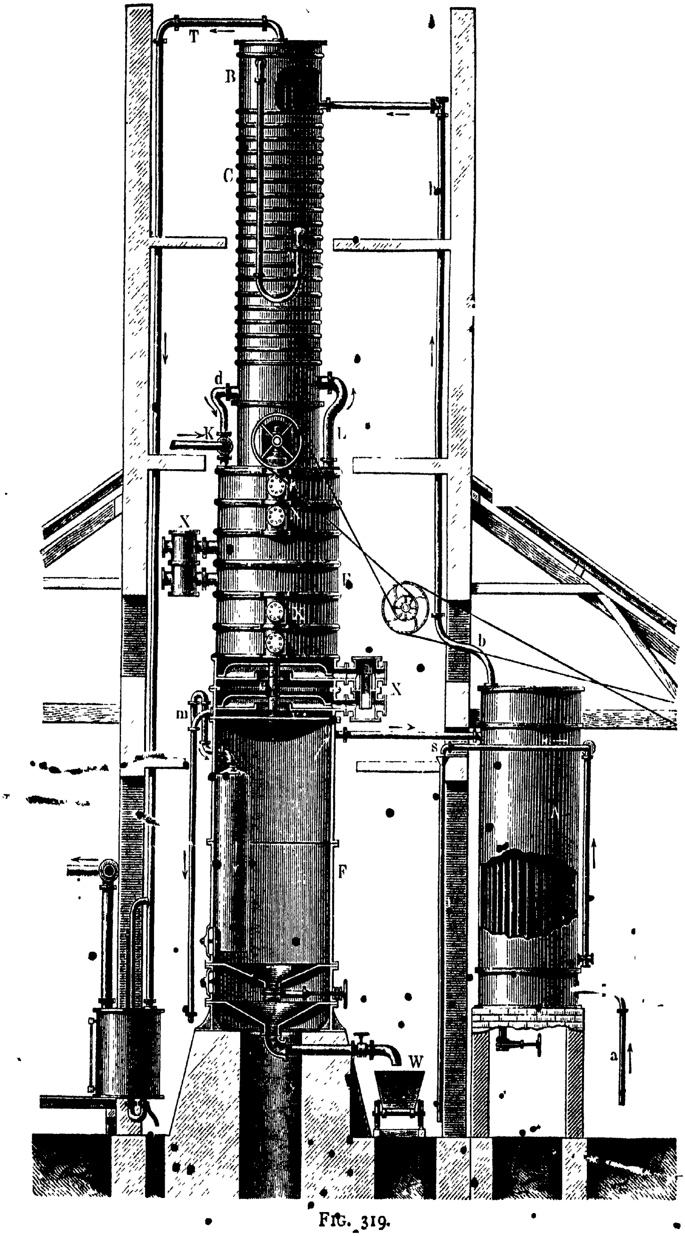

FIG. 319.

at its tenth chamber, and descends in this, in order to pass through the tube *d* into the agitating-column E. During this transit the volatile ammonium salts contained in the sewage are carried off by the hot vapours coming from E, and escape through L; the vapours pass through the rectifier C, where they become richer in ammonia, then through the analyzer B, where they give up the remaining water, and at last escape through T into the sulphuric-acid saturator. The uncondensable gases are carried under a fire-grate, to be burned. Before the sewage, deprived of volatile ammonium salts, enters through *d* into E, it is mixed with milk-of-lime pumped in through K, in the proportion of 8 kg. lime to each ton of sewage. The action of the agitating-column E is just the same as that described on p. 1446. The spent matter now descends through the siphon-tube *m* into the sludge-decanter F, 6 ft. 8 in. wide, where it suffers an enormous loss of velocity, which, along with the action of the lime on the albuminous substances, promotes a rapid settling of the solid impurities. By means of the two valves at the bottom, the sludge is discharged into the trucks W, and can be filter-pressed before being sent away. The clear liquid issuing from F is used for heating up the fresh sewage in A, as before described. The necessary heat is supplied to this apparatus by direct (wet) steam, through a 1¼-in. steam-pipe, *v*, just above the bottom of E.

This apparatus is capable of treating 65 tons of sewage per twenty-four hours. It is easy to clean, as all the overflow-pipes are arranged in outside annexes, X X, which are accessible by removing the flanges.

One of these apparatus has been in use since 1881 at La Tresne, near Bordeaux, and several others seem to be working satisfactorily in France.

Lencauchez's Apparatus

works under diminished pressure, and consists of two quite distinct parts. The one shown in Figs. 320 and 321 is called the "barometric chamber," and serves for expelling the volatile ammonium salts. It is a wrought-iron cylinder, A, 7 ft. 4 in. diameter and 11 ft. 4 in. high, fixed on the top of an iron column, B, of a height of 33 ft., at the bottom of which a siphon-pipe carries off the spent liquor into the tank C. In this "barometric chamber" a good vacuum can be kept up by an air-pump, which continually aspirates the gases and vapours given off by the sewage; this gaseous mixture is, as usual, absorbed in sulphuric acid, whilst the spent liquor runs

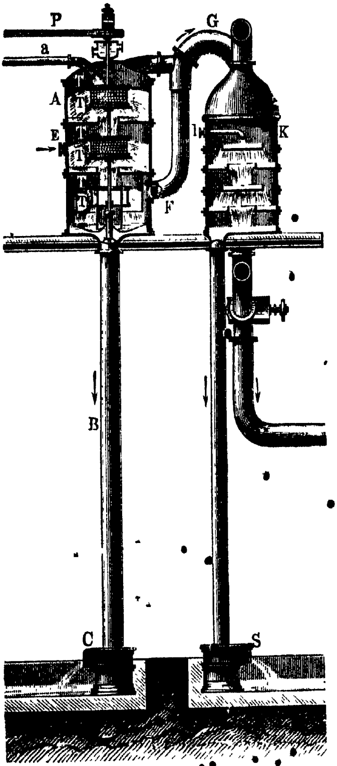

FIG. 320.

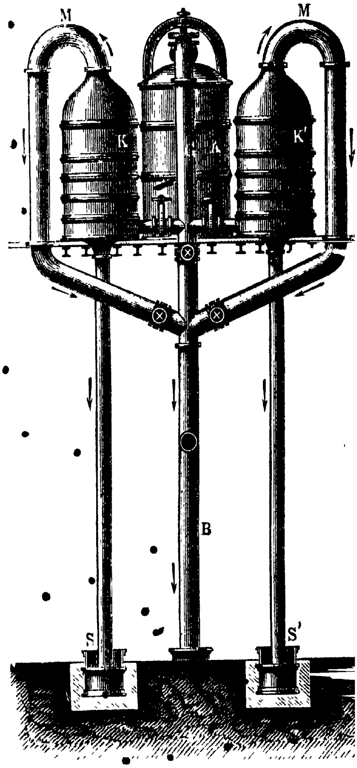

FIG. 321.

off at the bottom of the column B, in which the liquid rises equal to the atmospheric pressure. The chamber A is divided into three compartments, in which as many small turbines, T T T, set in motion by the pulley P, convert the sewage which arrives in the pipe *a*, three times over, into a fine spray, which greatly facilitates the escape of the volatile ammonium salts. The liquor is heated by means of the exhaust-steam of the engine, through the pipe E. The steam and vapours, issuing through F and G, pass alternately through one of two saturators, K K′, arranged on a principle similar to the chamber A. These are 6 ft. wide, and are provided with horizontal diaphragms for dividing the acid into a spray. The quantity of acid and the time it stays in the saturator must be so regulated that all the ammonia is absorbed and yet the acid is saturated. The solution of ammonium sulphate runs down the column and through the siphon S into a crystallizing-vessel. The pipes M and M′ carry off the noxious gases, which are aspirated by the air-pumps, freed from moisture by cooling down, and burned in the usual manner. The condensed liquid, which contains a little ammonium salt, is sent into the apparatus to be described next.

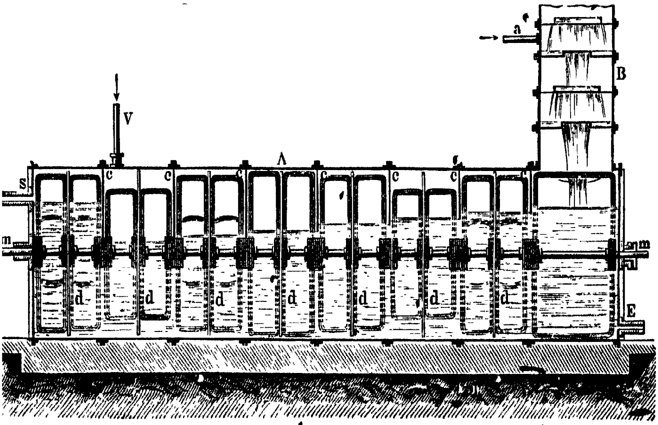

FIG. 322.

Fig. 322 shows that part of Lencauchez's apparatus which deals with the "fixed" ammonium salts. It is a horizontal cylinder, 10 ft. in diameter, and 33 ft. long, provided with a longitudinal shaft and agitating-paddles for mixing the liquor with milk of lime. Between the paddles there are seven disks for diminishing the speed of transit of the vapours. These seven partitions, *c c c*, divide the cylinder into eight chambers of equal size. The first partition from the left reaches down to the centre of the cylinder; the following ones are each 6 in. smaller than those preceding. A tube, V, enters the second chamber and injects into it the exhaust-steam from one or several steam-engines; the last chamber is surmounted by a cast-iron rectifying-column, B. The first plates of this column have simple holes, without covering-cups, so as not to be stopped up by solid matter projected from below; its upper portion is connected with two reflux-worms and a receiver for crude concentrated ammoniacal liquor. For making sulphate the worms are not cooled so much, and the vapours from them are conveyed into a sulphuric-acid saturator.

Into this apparatus the liquor, deprived in the "barometric chamber" of its volatile ammonium salts, is introduced through *a*, at the third chamber of the column B; it descends in thin jets, and gets into the horizontal cylinder, where it is mixed with milk-of-lime. The ammonia of the fixed salts is thus set free, and comes off gradually in the different chambers; it passes on successively from one to the other by bubbling through a mixture of liquor and lime, each time traversing a layer 6 in. deep. At last, after about half an hour, the liquor arrives totally spent at the other side of the cylinder and runs to waste by the siphon-tube S.

This apparatus is very ingeniously constructed, but seems too complicated, and has not made its way outside of France. It is doubtful whether the very much simpler means employed in England and Germany do not answer the same purpose quite as well.

Mylius (Ger. P. 66465) proceeds without distillation, by means of a vacuum. The sewage, clarified by lime, runs down upon cloths suspended in an evacuated chamber, where also sulphuric acid runs down asbestos-cloth and absorbs the NH_3. Seiffert (Ger. P. 71414) also employs a vacuum, in a column containing a number of dishes filled with sulphuric acid, on a similar principle to the last.

All processes for obtaining ammonia from sewage at the present time have hardly more than a sanitary interest, the great bulk of ammonia being supplied by the distillation of coal.

Absorption of the Vapours in Sulphuric Acid (Saturators).

The apparatus intended for this purpose, called the *saturator*, must be so constructed that, on the one hand, no ammonia escapes absorption in the acid, and, on the other hand, the gases set free (carbon dioxide and sulphuretted hydrogen) do not become injurious to the workmen and the neighbourhood. In describing a number of special apparatus we shall meet with various constructions of saturators; here we only mention the general principles to be observed.

Sulphuric Acid for Absorbing the Ammonia.

This acid is employed in a more or less concentrated state. Sometimes the gas, partly or mostly dehydrated by dephlegmation, is condensed in *dilute* sulphuric acid, so that no salt is separated during the saturation. The solution formed is clarified by repose, and is then evaporated, mostly in lead pans by means of a steam coil, up to crystallization, during which operation an offensive smell is given off. The mother-liquor is employed for diluting a fresh quantity of sulphuric acid. Another way of proceeding is to absorb the ammoniacal vapours in rather more *concentrated* sulphuric acid (say sp. gr. 1·4 to 1·45), in which case the ammonium sulphate separates in the solid state in the saturating-vessels, and is fished out of them from time to time. More acid is run in continuously in a thin jet, so that the saturator is always kept filled up to about the same level. The second process has the advantage of being continuous and saving all evaporation, but possesses the drawback that the liquor cannot clarify, and the salt does not come out so pure as in the first process.

In the style of working just mentioned, the concentration of the sulphuric acid used for feeding the saturators is usually about sp. gr. 1·45, and this is indeed the best way if the ammonium sulphate is intended for fertilizing purposes, in which case no pure salt is called for. Where, however, a greater purity of the ammonium sulphate is required, the saturation takes place in such a way that no crystallization sets in already in the receiver, but the resulting solution is filtered or otherwise purified, and only then evaporated to the crystallizing point. As a special instance of this way of proceeding we mention one observed by myself at an English factory, where the acid of sp. gr. 1·7, before use, was diluted with the same water, and saturated with ammonia up to a faintly alkaline reaction; then steam was blown through during half an hour in order to remove the hydrogen sulphide and avoid its causing inconvenience later on. The solution was then concentrated in pans lined with lead (1·8 lb. per superficial foot), 8 ft. diameter, and 2 ft. deep, by means of steam of 2 atmospheres passed through in a lead coil. The sulphate thus obtained was drained, and the mother-liquor added to another charge of acid for the saturator. Such a proceeding is, of course, only rational, where either pure ammonium sulphate is called for, or where dilute sulphuric acid, produced by some other chemical process, is at disposal at a particularly low price.

The sulphuric acid arrives at the factory in tank-wagons, tank-boats or carboys, and is in the first instance mostly discharged into iron cylinders, placed on the ground or lower down, from which it is forced by means of compressed air into store tanks, placed at a high level, in the way described in Lunge's *Sulphuric Acid and Alkali*, fourth edition (1913), i., pp. 813 *et seq.* The store tanks should be placed in a room the temperature of which never sinks below 5° C., because at lower temperatures crystals of sulphuric acid would be formed which might stop up the taps, pipes, etc. The pipes for conducting the acid to and from the store tanks, measuring vessels, saturators, etc., are made of strong lead; the taps are made of stoneware, strengthened by "regulus metal."

A point of importance is the *quality of the acid employed.* In England, frequently, *sulphuric acid made from brimstone* is used in the manufacture of sulphate of ammonia, because pyrites-acid contains iron and arsenic, both of which discolour the sulphate. F. C. Hills (B. P. 3257, of 1878) avoids this by allowing the pyrites-acid to meet with an excess of ammonia, which precipitates iron and arsenic (?); the excess of ammonia is absorbed in another vessel, in the manner described in the patent. In Germany nothing but *pyrites-acid* is used; the resulting sulphate has a grey tinge, but it is as valuable for manure as the best white. Such grey sulphate is also very commonly found in England. The pyrites-acid ought, however, to be made from pyrites containing very little arsenic; that made from Spanish pyrites (which is now practically the only one used in England, and is often employed in Germany as well) is objectionable because it contains too much arsenic, which produces yellow sulphate—a colour not at all liked by the consumers. Some German makers produce white sulphate, even from strongly arsenical acid, by *skimming off the arsenic trisulphide* from the top of the saturator, which, of course, necessitates an open form of this apparatus. W. A. Meadows (B. P. 5520, of 1884) purposely adds a small quantity of tar, pitch, oil, fat, or the like, and carries on the operation at a temperature not below 38° C. In this case a scum is formed on the top, which contains the arsenic and iron of the sulphuric acid, and facilitates their removal. An American patent by E. A. Falls (No. 318972) covers the same invention. A much better process, which I saw at a Dutch factory, where it had been in use most successfully for a number of years, is the following:—Ordinary pyrites-acid is used, of sp. gr. 1·71. To this a certain quantity of "*vitriol-tar*" is added; that is, the sulphuric acid which has served for washing crude benzol, and which is charged with a large quantity of tarry impurities (p. 878). On the saturation of the acid by the ammonia coming over, the tarry matters are precipitated and rise to the surface, carrying along and enveloping the arsenious sulphide formed at the same time from the pyrites-acid. The scum is carefully removed, and the sulphate fished out after this is perfectly white, as I could see from the large quantity kept in stock. Thus the "vitriol-tar," which formerly was an intolerable nuisance, is utilized not merely for its acid, but even its tarry impurities are made to serve a very useful purpose (*cf.* Cooper, *Chem. Trade J.*, 1916, lviii., p. 233). A similar, but much more complicated, patent process has been previously described.

The prejudice against pyrites-acid seems to be likewise decreasing in England. At least at one of the very largest ammonia-works the author was told that they used it as well as brimstone-acid; the sulphate made from the former was somewhat discoloured, but fetched exactly the same price as the white sulphate made from brimstone-acid.

In the majority of cases the sulphuric acid is bought at a concentration of 142° Tw., corresponding to about 78 per cent. H_2SO_4; only in cases where it has to be got from a considerable distance, it will pay to buy the highly concentrated acid of 166° to 168° Tw. = 92 to 95 per cent. H_2SO_4, or more. On buying it, the condition should be made that the acid should contain as little as possible arsenic and nitrous acid. The testing methods are described in Lunge's *Sulphuric Acid and Alkali*, fourth edition (1913), i., pp. 368 *et seq.*, and in his *Technical Chemists' Handbook*, 1910, pp. 135 *et seq.*

The *quantity of sulphuric acid required* is given by the molecular weights as follows:—

$$98 \text{ parts } H_2SO_4 + 34 \text{ parts } NH_3 = 132\ (NH_4)_2SO_4.$$

Hence 100 parts ammonia require: $\frac{98 \times 100}{34} = 288{\cdot}2$ parts real H_2SO_4, equal to $\frac{288 \times 100}{78} = 369{\cdot}4$ parts sulphuric acid of 142° Tw.

Saturators for absorbing the Ammonia in Sulphuric Acid.[1]

The saturators differ in form as follows:—Those intended for dilute acid are closed tanks lined with lead, partially filled with sulphuric acid; the ammoniacal vapours arrive in a pipe, which branches out at the bottom at the tank, and is there provided with many holes for the issue of the ammoniacal vapours. The gases liberated by the decomposition, along with a large quantity of steam generated by the heat of the reaction, are conducted away by a pipe from the upper part of the vessel, and are disposed of in various ways, to be described hereafter. The passage of vapours into the vessel is continued until a sample, drawn from a tap, shows that the acid is sufficiently saturated. It is best to leave a slight excess of acid, in which case the liquor, after evaporation in leaden pans by indirect steam, yields whiter sulphate.

For more concentrated acid another form of saturator is used, consisting of a tank not completely closed, to which, as the acid becomes saturated, more strong acid is added, either from time to time or in a continuous thin jet. The waste gases and steam in this case are drawn away from the closed part of the tank by means of chimney-draught, which must be strong enough not to allow any gas to escape out of the open portion; this can be still better secured by a fan-blast or an injector. As the solution becomes supersaturated with ammonium sulphate, this salt crystallizes out, in spite of the heat. In some cases this is continued till the liquor becomes too thick, whereupon the whole contents of the saturator are drawn out by means of a bottom tap into a cooler, from which, after the crystallization is complete, the mother-liquor is pumped or ladled back again into the saturator. In other cases the salt is fished out of the saturator during the operation itself. This is done in a "fishing-box," shown in Fig. 323. It consists of a wooden vessel lined with lead, and divided into two compartments by

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[1] Cf. *supra*, p. 1424, as to continuously acting saturation.

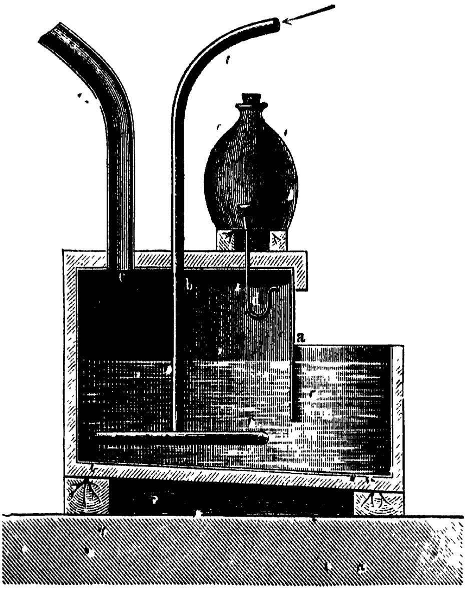


FIG. 323.

the lead curtain *a*, which dips into the acid. The outer compartment is lower and open at the top; the bottom is made to slope to this side. The other compartment is closed by a lid, perforated for the tube *b*, through which the ammoniacal vapours arrive, for the exit-pipe *c*, and the acid-pipe *d*. The sulphate precipitating during the operation is raked towards the open end, and fished out there from time to time by a perforated ladle. The best form is that in which the bottom of the open compartment is made into a well, in which fits a strainer; the salt drawn from the closed compartment falls into this strainer, which from time to time is lifted out to empty the salt. Fig. 324 shows this arrangement.

A saturator constructed on this principle, which has long been well known to practical men, and has been in use at many works (it is also described and figured in my German work of 1867), has been patented by W. Arrol and J. Meikle (B. P. 12174, of 1884). The only novelty their patent contains is that their vessels are not made of lead, but of copper—an invention not likely to be infringed by others.

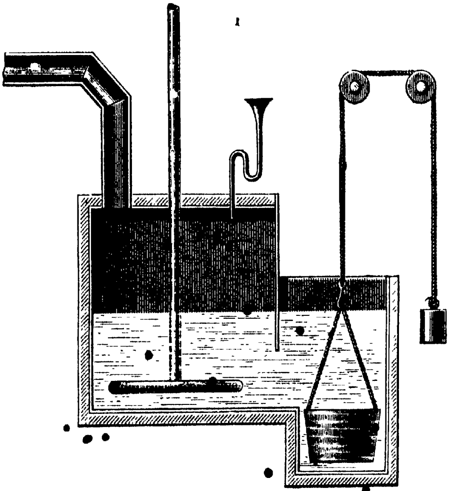


FIG. 324.

Watson Smith (priv. comm.) recommends the following plan for obtaining perfectly white sulphate:—The saturator is charged with acid of 80° Tw., and ammonia is passed in until there is a slight smell of it. The excess is neutralized by a little acid; and the separated sulphate is *at once* fished out, whereupon the operation is commenced again. If, however, the acid is run in little by little, and the gas passed through for a long time, the separating sulphate is black; and so it is in the former case, if, when the liquor has been proved by its smell to contain an excess of ammonia, fresh acid is run in and fresh gas is passed through, without fishing out the sulphate already formed, so that it is allowed to accumulate.

In fact the rule is, to fish out the *freshly deposited* sulphate from *tolerably acid* mother-liquors. The fishing is done by means of a ladle of galvanized iron, perforated with numerous small holes; the sulphate is thrown upon a lead-lined drainer, from which the mother-liquor runs back into the saturators.

In the case of discontinuous saturators, it should not be forgotten that solutions of ammonium salts, when boiled, give off some free ammonia. Hence the acid, when nearly saturated with ammonia, hot as it is, will not completely retain it, especially if the bubbles of gas are rather large. For this reason the points of contact should be multiplied, and the gas-pipe should not dip too low into the acid. In the case of very large apparatus, it might be best to employ two saturating-boxes in succession, the upper one to be charged with fresh acid; the gas would have to pass first through the lower box, where it would give up nearly all its ammonia, the rest being absorbed in the upper box. When the contents of the lower box have been run off, those of the upper box should be run down into it, and fresh acid charged into the upper saturator.

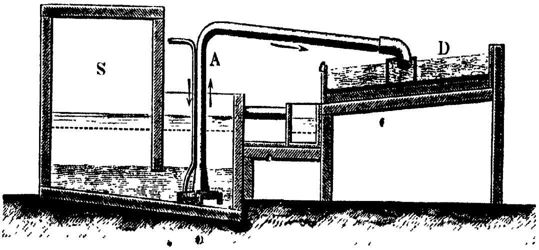


FIG. 325.

The reaction between the ammonia and the sulphuric acid produces so much heat that the liquid soon reaches nearly its boiling temperature. This, in the first instance, causes a very welcome, constant agitation; secondly, it prevents the condensation of steam and keeps the liquid at higher concentration.

Wilton's apparatus (Ger. P. 54827; *Gas World*, 1890, p. 717) is shown in Fig. 325. The sulphate formed in the saturator S is continuously lifted by the injector A on to the draining-plate D, from which the mother-liquor runs back into the saturator. This arrangement saves much labour. Four saturators can be supplied by one ejector, which throws out 26 tons of sulphate per day, and the regular removal of the salt admits of raising the production of the stills by 20 per cent.

Sauer (Ger. P. 70185) (Figs. 326 and 327) passes the ammonia through a_1 *b* into the saturator *c*, the H_2S escaping from the bell *d* through pipe d_1 into the dust-collector d_2, and thence into the chimney or into a purifier. The sulphate is not fished out, but acid is generally run from box *c* through funnel *e* into the bell, until all is saturated. The ammonia is now passed into another saturator, tap a_2 is closed, and the salt fished out of the first saturator.

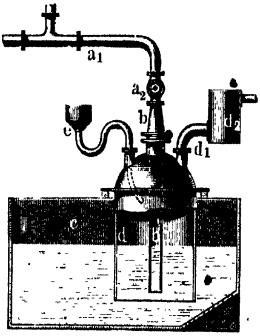


FIG. 326.

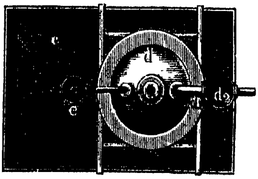


FIG. 327.

Kennedy (B. P. 1653, of 1890) describes some improvements in ordinary saturators with slanting bottoms.

Colson's saturator (*Alkali Inspectors' Report*, No. 32, p. 63) has a conical bottom of the proper shape, as shown here (Fig. 328), and a simple outlet-valve, consisting of a copper disk pressed against the mouth of the outlet-pipe by means of a screw. The vessel is made of cast-iron with lead lining. The valve is fixed in such a position that the salt is removed as soon as it forms, as shown by the inspection-pipe in the middle of the saturator.

Ellery's saturator (*Gas World*, 1895, p. 783) (Fig. 329) is very similar to the above, but is made of wood lined with

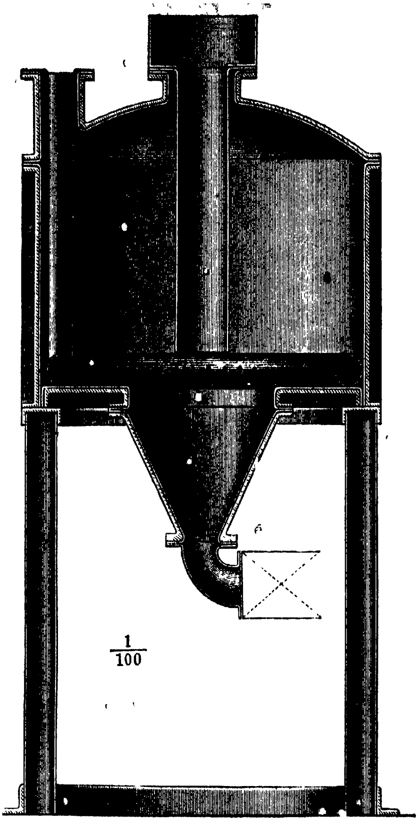


FIG. 328.

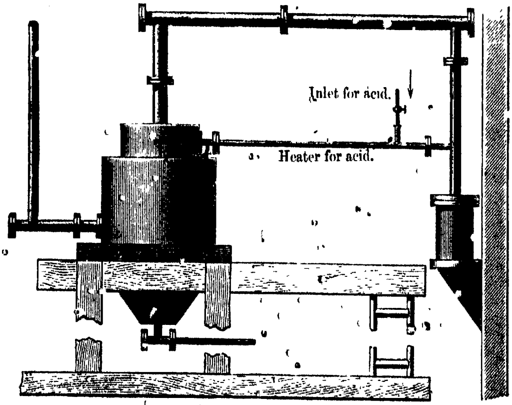


FIG. 329.

lead, with a simple trap-valve at the bottom. The acid is heated up before entering the saturator by the hot waste gases.

Carulla (*J. Soc. Chem. Ind.*, 1903, p. 607) points out that the saturator should be provided with safety-valves, the absence of which once caused an accident at his works.

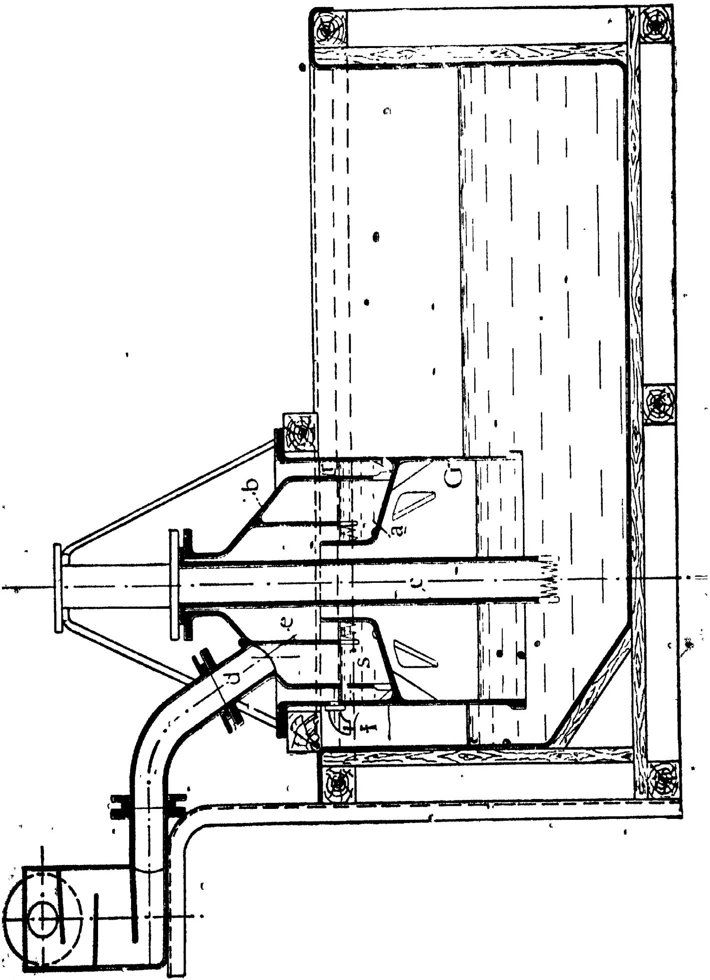
Julius Pintsch, Aktien-Gesellschaft (Ger. P. 134976), improve the ordinary bell-saturator by providing a perpendicular partition, on one side of which the acid is run in, the other side containing several slanting plates which force the gases to make a circuitous route and to give up all the ammonia to the acid.

Marriott (B. P. 4730, 1891) removes the ammonium sulphate from the saturator by means of an endless belt of wire gauze.

Duggan (B. P. 5011, 1896) describes again the well-known arrangement, according to which the upper part of the separator is cylindrical, while the lower part is conical or curved, to promote the discharging of the sulphate.

Ballantyne (*J. Soc. Chem. Ind.*, 1903, p. 794) keeps the whole apparatus under a vacuum. All overhead tanks can thus be dispensed with, as the liquor and the acid can be drawn into the still and saturator from any place a little above the floor level. He finds that the best time for "salting out" is when the liquid in the saturator is at 56° to 57° Tw. The vacuum on the pump and saturator should be 23 to 24 in., and that on the still 13 to 15 in. of mercury. The total consumption of fuel is 4 cwt. of coke per ton of ammonium sulphate. For the saturator he uses a special discharger (B. P. 27070, of 1902), which at its neck has a seating against which an upwardly closing cone, attached to a vertical spindle passing through a stuffing-box in the bottom, can be screwed up by mechanical means. When the discharger is full of crystals, the valve is closed, and a sliding door is moved upwards to admit of removal of the contents of the vessel.

Schwab (B. P. 17585, of 1903) avoids the drawbacks attached to cast lead or iron saturators by employing a saturator with body and top made in one piece of lead, with a fender attached to the body, a bottom extending under the body and fender, and an aperture formed at the base of the body, making a passage between this and the fender. This and the body may be formed out of one sheet.



Heuss (priv. comm.), instead of lead or lead-covered iron, employs saturators made of earthenware, capable of resisting both acids and changes of temperature.

Rosenkranz (*J. Gasbeleucht.*, 1904, p. 459; *J. Soc. Chem. Ind.*, 1904, p. 602) employs two saturators in rotation, so that the acid in one of these can be completely saturated in the first, and the remaining NH_3 completely absorbed in the second, whereupon the gaseous current is reversed, so that the second saturator now comes first.

Ledig (Ger. P. 71577) provides the saturator with a mechanical stirring apparatus. Neumayer (Ger. P. 24511) converts the acid into a spray; so does also Wellstein (Ger. P. 28762). A special apparatus for that purpose is described by Heuss in Ger. P. 227946.

Zimpell (Ger. Ps. 161718 and 170807; B. Ps. 6891 and 23379, of 1904; U.S. P. 782637) recovers the ammonia not absorbed the first time by a second saturator combined with the first, on the following principle:—When dry vapours of water and NH_3 are passed through the first saturator, no water is condensed in the liquid form, since the heat produced by the combination of the NH_3 and the acid keeps the steam at a sufficiently high temperature. In the second saturator, however, where but little heat is generated, there is a constant condensation of water and consequent dilution of the acid. To prevent this, the inventor combines both saturators to one apparatus, as shown in Fig. 330. It is a combination of two bells, in such a way that the crown *a* of the lower bell G forms the floor of the upper bell *b*. Above this floor there is a scalloped wall *e*, which acts like the dipping tube in an ordinary saturator. The gases issuing through pipe *c* from the lower principal saturator, before being carried away through *d*, play round the upper saturator and keep it at such a temperature that no steam is condensed to liquid water. This apparatus is built by the Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft ("Bamag").

The following data give comparative results with an ordinary saturator and bell and with Zimpell's double bell. The liquor used in both was the same, 1·18 to 1·19 per cent., and was fed in equally; the acid was a mixture of saturated acid with fresh acid of 58° Baumé. The ammonia in the waste gases was determined by cooling them to 26° C. and finding the amount of ammonia in the condensates. With the old apparatus, the loss went on rapidly increasing from hour to hour; with the new, it remained very uniform for some hours and then fell off. In more detail, we have—

	Old Apparatus.	New Apparatus.
Liquor treated, cubic metres	8·150	10·100
NH_3 therein, kilograms	96·985	119·180
NH_3 run off in the liquor, kilograms	0·235	0·292
NH_3 passed into sulphate plant, kilograms	96·750	118·888
Loss in the saturator, kilograms	6·367	0·773
Loss, percentage of NH_3 passed in	6·575	0·650
Duration of experiment, hours	9½	12
Loss of NH_3 in third hours, kilograms	0·089	0·082
,, ,, sixth ,, ,,	0·388	0·095
,, ,, ninth ,, ,,	1·554	0·102
,, ,, twelfth ,, ,,	—	0·015

The contents of the supplementary saturator were kept at sp. gr. 1·45 to 1·52 by addition of acid, the excess overflowing into the saturator proper; this was emptied out every six or seven hours. The sulphate from the new apparatus was brighter than that from intermittent saturation, and it contained less arsenic and iron, which were easily removed with the froth on the acid in the supplementary saturator. The acid removed from the saturator proper and separated from sulphate by draining or centrifugalling could be used over again, not having been diluted.

An acid-saturator, constructed by the Berlin-Anhalt. Masch.-Akt.-Ges. (Ger. P. 165308) provides a plate with nicked margin, which can be raised or lowered for closing the inner bell. During the work this plate is lowered, and forms a gas-lute, but it is raised when fresh acid is run in. Other forms of saturators are described in their Ger. P. 233518.

Clarke, Chapman & Co. and Robson (B. P. 27840, of 1905) employ for the absorbing-acid a closed tank divided by partitions which must be passed by the gases in a zigzag way.

On a similar principle are constructed the apparatus of Brotherton and Wyld (B. P. 14349, 1908) and of E. Wagener (Ger. P. 216069).

Langlands and O'Connor (B. P. 17267, of 1905) construct the absorbing-vessel of porcelain or enamelled stoneware, using lead only for connecting pieces.

Williams and Fenner (B. P. 25547, of 1906) fix a distributing-pipe for steam and ammonia externally to the saturator, communicating with it by means of a number of symmetrically placed short connecting-pipes. In this way the sulphate is formed equally throughout all parts of the acid liquor, and incrustations are avoided.

Schulte (Ger. P. 288497) surrounds the gas-entrance pipe, dipping into the liquid, by another pipe; in the circular space between these two pipes the gases rise upwards and get thoroughly mixed with the liquid.

A saturator constructed by Hartmann is described by Peters in *J. Gasbeleucht.*, 1906, p. 164.

Thiel (Ger. P. 193218) employs an apparatus consisting of two bell-saturators. The gases first pass through the upper one, and from the top of its bell they pass on to the lower saturator, where they have once more to pass through sulphuric acid. This lower saturator has a double leaden bell. Openings are provided which ensure a good circulation below and outside the lead bells, without allowing the gases to escape below their bottom. The inner bell is kept at a temperature above the boiling point of water; the outer one is much colder. This produces a circulation of the liquid in this saturator.

Brunck (B. P. 8287, of 1903; Fr. Ps. 331077 and 356589) provides his saturators with a number of "dipping elements."

Rothermund and the Aktien-Gesellschaft für Kohledistillation, Düsseldorf (U.S. P. 1067843), employ a saturator, divided into two halves by a partition not reaching down to the bottom. The gases, cooled and freed from tar, enter into one of these halves; the other receives the ammonia-containing vapours driven out of the gas-water obtained by cooling, and hot fire-gases or air for expelling the water condensing here.

Koppers (B. P. 834, 1913; Ger. P. 272601) passes a portion of the ammoniacal vapours into the upper part, the other part of the vapours into the bottom of the saturator, close to the place whence the solid sulphate is taken from, thereby securing the formation of a neutral salt without loss of ammonia. The excess of ammoniacal gas entering here completely saturates the acid liquor descending from the top, and at the top the excess of acid retains the last portions of ammonia.

Wagener (Ger. P. 234688) protects the upper part of the saturator against loss of heat by an insulating coating, and, on the contrary, cools the lower part by outside rinsing with water.

C. Otto & Co. (Fr. P. 459219) employ a cylindrical saturator with a truncated conical bottom, provided with an overflow and an ejector which transfers the deposited sulphate to a funnel-shaped vessel, placed higher up, from which the mother-liquor is returned to the saturator.

Barnick (*Chemische Apparatur*, 1915, ii., p. 61) describes a plant for the manufacture of ammonium sulphate, in which the concentration of the sulphuric acid is so chosen (=55 per cent. H_2SO_4) that, divided by the heat of neutralization, steam is constantly evolved and the ammonium sulphate crystallizes out as it is formed, and can be continuously removed.

The "Bamag" (Ger. P. 279134) treat the condensing liquid, obtained in the "direct" process for producing ammonium sulphate, with sulphuric acid, before introducing it into the saturator, while still hot, whereby the ammonium chloride present therein is converted into sulphate; the hydrochloric acid evolved covers the expense of the process.

P. von der Forst (Ger. P. 280652) passes the NH_3 produced in distilling gas-liquor before entering into the ammonia saturator, through a vessel containing a copper salt, where cupric cyanides are formed; these, when being treated with dilute sulphuric acid, pass over into a solution of ammonium sulphate.

The saturator of Plzak (Ger. P. 189473) is divided by partitions, and the compartments thus formed are charged with acids of different concentration. The gases are first passed through weaker acid, which absorbs most of the ammonia, and then through strong acid. After some time some acid is run from the latter into the former compartments, and is replaced by fresh acid.

Koppers (Ger. P. 181846) prevents dilution of the bath in the saturator by reheating the gases from a still, which had been previously cooled for the purpose of separating the tar, by means of the excess heat of the crude gas or other waste heat.

Feldmann (B. P. 11525, of 1902; Ger. P. 134976) arranges a second saturator over the first, connected with it by an overflow, opening into the bell of the lower vessel, which is thus supplied with relatively fresh acid. A similar principle is employed by Koppers (Ger. P. 140350).

Chatfield (Ger. P. 82443) employs technical "nitre cake" (the residue from the manufacture of nitric acid, consisting of an impure sodium hydrosulphate) for the absorption of ammonia.

Pallenberg (B. P. 5657, of 1908) covers the lead coating of the saturator with plates of acid-proof material, bound by means of an acid-proof binding medium. The bell or partition-wall of the saturator may be constructed entirely of such material, but in this case the crown or cover of the bell is attached loosely with putty to the cylindrical portion, with an outer cover, bolted on, keeping the whole right, and yet allowing each part to expand individually; cracking of the bell is thus avoided.

Frerichs (U.S. P. 905415, of 1908) combines ammonia with ammonium hydrosulphate and heats the normal ammonium sulphate thus formed so as to give ammonia again, and acid-ammonium sulphate or pyrosulphate to be re-used in the process. If the ammonium sulphate contains nitrogenous and other carbon compounds, it may be purified by heating the impure salt in a blast of air to such a temperature that the volatile carbon compounds are volatilized or oxidized, and the nitrogenous compounds are converted into ammonium sulphate by reacting with the sulphuric acid of the ammonium salt.

Erlenbach (Ger. P. 203309, 10th Jan. 1908), in order to retain the ammonia coming from the saturator when the acid is nearly saturated, allows these gases to meet the sulphuric acid intended to flow into the saturator. This had been done previously, but if, as hitherto usual, the acid is at the strength required for the process within the saturator, the temperature rises too high in the lead-lined apparatus where the gases meet this acid, and the lead lining is rapidly destroyed. This is avoided by employing only a portion, say one-fifth, of the sulphuric acid for the purpose in question; running four-fifths straight into the saturator, diluting the last fifth with rather more than its weight of water, and employing this dilute acid for absorbing the NH_3 escaping from the saturator. The temperature in this case never rises above 109°, and the NH_3 is completely retained.

Chur (Ger. P. 277379) enriches the gases, after removing the tar, by fresh concentrated ammoniacal liquor (obtained by passing gas-liquor through a boiler, provided with a reflux-cooler), whereby the gases going into the saturator are sufficiently heated to dispense with further heating.

The Soc. Lorraine de Carbonisation (Fr. P. 454246) employs a vertical bell-jar, immersed in the liquid of a saturator, provided with perforations.

Hilleke (U.S. P. 1163753) provides the saturator with a cylindrical baffle, to the upper part of which is attached a circular trough for supplying the acid.

Absorption of Ammonia as Sulphite.

Sulphur dioxide has been employed for absorbing ammonia, afterwards converting the sulphite into sulphate by the action of air, partially or entirely, by Laming, in 1852; by G. E. Davis (*J. Soc. Chem. Ind.*, 1883, p. 521); by Addie, for absorbing ammonia direct from blast-furnace gases (p. 175); by A. M'Dougall (B. P. 15496, of 1884), who passes kiln-gases from sulphur- or pyrites-burners into an ordinary saturator, and oxidizes the crystallizing ammonium sulphite to sulphate, while the mother-liquor, containing sulphite as well, is used for scrubbing coal-gas, in which case it absorbs ammonia and decomposes the hydrogen sulphide with precipitation of sulphur; and by Deck (B. P. 17050, of 1887).

Collett and Eckardt (Ger. P. 268497) and E. Collett (Ger. P. 283161) oxidize the ammonium-sulphite solution by running it down in a scrubber through which air is pumped in a circulating stream in such a way that the gas escaping from the apparatus contains about 10 per cent. oxygen. The B. P. is 16629, of 1911; the U.S. P. 1052797.

Burkheiser (Ger. Ps. 236757 and 256341) oxidizes the ammonium sulphite by subliming it in a current of hot air.

Fritzsche (Ger. P. 256400) causes SO_2 to act on alumina, oxidizes the aluminium sulphite into sulphate, and converts this by ammonia into ammonium sulphate.

Barth (Ger. P. 235157) converts the H_2S, expelled from gas-liquor, into SO_2, and utilizes this for the absorption of NH_3.

Bambach (Ger. P. 279953) decomposes the sulphates of alkaline earths by neutral or acid ammonium sulphides, or the components thereof.

Young (B. P. 1310, of 1880) conveys the ammoniacal vapours, evolved without using lime, not through a saturator, but along with air through a fireplace, where the ammonium sulphide is partly burned into sulphite and partly into sulphate, which are conveyed into a suitable condenser. The ammonium sulphite is converted into sulphate by passing a current of heated air through the solution (as previously proposed by Laming). Since the gas-liquor never contains enough sulphides to convert all the ammonia into sulphate, sulphur dioxide is mixed with the products of distillation before or after they have passed through the fire, or else the condensed liquid is saturated with sulphurous or sulphuric acid. This process is evidently altogether analogous to that patented by Messrs Addie for blast-furnace gases (*supra*, p. 175): it has the disadvantage, however, that at the high temperature employed much ammonia will be burned, and that the condensation of the highly heated ammonia compounds diluted with air is not an easy matter.

Hemingway (B. P. 9432, of 1899) burns part of the H_2S evolved in the manufacture of ammonium sulphate and scrubs the SO_2 produced in a coke-tower, to the upper part of which ammonia is admitted, passing on the surplus SO_2 to a second tower. The ammonium sulphite is decomposed by ferrous sulphate into a mixture of ferrous sulphite and ammonium sulphate, which in a third coke-tower is treated with another part of the H_2S originally evolved. In this tower FeS and S are deposited as solids, and the solution of ammonium sulphate is run off from the bottom. *Cf.* also *Alkali Inspectors' Reports*, No. 35, p. 142, and No. 36, p. 172, concerning experiments on a continuous removal of sulphuretted hydrogen by means of manganese salts and oxygen.

Stutzer (Ger. P. 255439) allows air or oxygen under an increased pressure of one or several atmospheres to act upon ammonium sulphite at a temperature at which vigorous dissociation of ammonium sulphite takes place.

The Chemische Fabrik Pommerensdorf and R. Siegler (Ger. P. 281095) absorb ammonia from gases, vapours, etc., by mixing them with sulphur dioxide and recovering the ammonium sulphite in the form of a concentrated aqueous solution by drawing the mixture by means of a centrifugal fan, into an atmosphere saturated with moisture, cooling being avoided; the NH_3 and SO_2 still contained in the exit-gases are recovered as ammonium sulphate by passing the gases through a wooden tower packed with wood charcoal or coke.

The Badische Anilin- und Sodafabrik (Fr. P. 463487; B. P. 12979, 1913; Ger. Ps. 270379, 270574, 273306, 273315, and 276490) treat a concentrated, slightly ammoniacal solution of ammonium sulphite at about 80° with air under a pressure of 20 atmospheres or more, in the presence of a catalyzer, such as porous earthenware impregnated with manganese hydroxide. The U.S. P. 1091234 of Mittasch and Morawitz, assigned to the Badische, is for the same process.

The same firm (B. Ps. 12845 and 14114, of 1914; U.S. P., of Bosch, 1106919) heats ammonium bisulphite in aqueous solution at an initial temperature of 50° to 100° in the presence of a catalyst, preferably sulphur; other catalytic substances—selenium, tellurium, arsenic, or their compounds—and many other substances are also applicable. Several modifications of this process are described.

Their Ger. P. 270379 (U.S. P., of Bosch, 1133086) describes the conversion of ammonium bisulphite into sulphate, by passing the solution through tubes, heated to 150° under pressure.

Their Ger. P. 270574 shows that by adding to aqueous solutions, in which the bisulphite has been converted into sulphate, more normal or acid sulphite, the sulphate is made to crystallize out.

Pure ammonium sulphate is obtained by Tufts (U.S. P. 1065066, assigned to the Semet-Solvay Co.) by rapidly heating crude ammonium sulphate so as to drive off ammonia with its accompanying impurities, leaving ammonium hydrosulphate behind. The evolved ammonia is separated from the volatile impurities and recombined with the acid salt to form pure normal ammonium sulphate.

Other Ways of producing Sulphate of Ammonia.

Cobb (Ger. P. 275453) treats gases, containing ammonia and sulphur compounds, with the solution of a metallic sulphate, obtains the ammonium sulphate thus formed from the solution, and regenerates the precipitated sulphide to sulphate by roasting and treatment with air.

Vis (B. Ps. 9699, 1911; 2002, 1912; 2462, 1914; U.S. Ps. 1152244 and 1152245; Fr. P. 427067) prepares ammonium sulphate by the interaction of NH_3, CO_2, and $CaSO_4$ in a saturated solution of ammonium sulphate.

La Suburbaine, Soc. an. (B. P. 4687, 1914), carries the ammoniacal vapours into a chamber in which an acid fog is produced.

Mackenzie (B. P. 10059, 1914; U.S. P. 1155753) produces ammonium sulphate directly from the ammonia and the sulphur compounds contained in coal-gas. This gas, after removal of the tar, is passed in a moist state, together with a nitrogen oxide, at about 93° into a vessel, where the sulphur compounds are oxidized and ammonium sulphate is formed. The excess of nitrogen oxides is absorbed in sulphuric acid of 70 to 80 per cent.; the coal-gas is ultimately purified by lime.

Duvieusart (B. P. 17475, 1915) washes the coal-gas with a solution of sulphited organic bases, obtained from tar or tar-oils by treatment with sulphurous acid, and heats the solution, whereupon ammonium sulphate is produced.

Still (B. Ps. 28072, 1912, and 28245, 1913) obtains ammonium sulphate directly from coal-gas by cooling, saturating, and heating in a tower.

P. E. Williams (B. P. 2841, 1914) prepares ammonium sulphate from sulphocyanides, *e.g.*, ammonium sulphocyanide, such as it is formed in the manufacture of coal-gas, by heating with an alkali or alkaline earth in the presence of water, removing the CO formed, evaporating the solution to dryness, mixing and covering it with lime-mud, heating to 500° to 600° in the presence of water or steam, and absorbing the escaping ammonia in sulphuric acid.

Schuster and British Coke Ovens, Ltd. (B. P. 6061, 1914), distil gas-liquor by gas withdrawn from the main, after removing the tar and reheating, and return the resulting mixture of gas and NH_3 to the gas-main at a point where the pressure is lower than that of the gas containing ammonia, and pass the whole to a saturator.

J. W. England (B. P. 26429, 1911) passes the NH_3 gas into a solution of iron sulphate and separates the resulting iron oxide from the solution of ammonium sulphate formed.

Layman & Co. (Ger. P. 244924) obtain ammonium sulphate immediately in a solid form from coal gas by exposing this to lignite dust, soaked with sulphuric acid. Since in consequence of the heat produced by the formation of the sulphate the lignite is destroyed, technical ammonium sulphate is thus obtained without any further treatment. [It is, however, doubtful whether this process will pay, since a considerable amount of sulphuric acid will be decomposed by the action of the lignite at higher temperatures.]

Easterfield (Ger. P. 160402) prepares a concentrated solution of ammonium sulphate by treating ammoniacal liquid with calcium sulphate and returning the resulting solution to a gas-washer.

The Verein chemischer Fabriken at Aussig (Ger. P. 280967) prepare ammonium sulphate by heating ammonium nitrate with an excess of sulphuric acid, so that the distillation is finished below 152°; this yields almost the theoretical quantity of very pure nitric acid, and the residue, after being neutralized with ammonia, is marketable ammonium sulphate.

The Badische Anilin- und Sodafabrik (Ger. Ps. 281174 and appl. B69749) prepare ammonium sulphate by passing gases containing NH_3 and CO_2 through an aqueous mud of calcium sulphate, kept in continuous motion, separating the slime of calcium carbonate from the solution of ammonium sulphate by "immersion filters," and heating the slime to expel the ammonia retained, which is recovered by condensing the vapours.

Their B. P. 27962, of 1913 (communicated to J. Y. Johnson; Fr. P. 466302), states that it is well known that by treating calcium sulphate (*e.g.*, gypsum) with either a dilute or a concentrated solution of ammonium carbonate or bicarbonate, double decomposition takes place, resulting in the formation of ammonium sulphate and calcium carbonate. If ammonium bicarbonate is used, it may be necessary to complete the decomposition of the calcium bicarbonate formed, *e.g.* by heating the mixture. Hitherto this simple reaction has been but little used, owing to the difficulty of separating the fine precipitated calcium carbonate from the ammonium sulphate solution, and of completely recovering the ammonium sulphate from the calcium carbonate mud. Filter-presses, etc., are in this case of little value, on account of the large quantity of water required for washing the precipitate, and the cost of evaporating this water; further, the calcium carbonate is incompletely washed out, so that some ammonium sulphate is lost. The patentees claim as their invention (1) the manufacture of ammonium sulphate practically free from calcium salt, by treating calcium sulphate with ammonium carbonate or bicarbonate in the presence of water, then filtering the solution so that the calcium carbonate sets on the filtering surface in a continuous adherent layer of uniform permeability, and then washing it with water until it is practically free from ammonium sulphate. (2) The manufacture of ammonium sulphate practically free from calcium salt, by treating calcium sulphate with ammonium carbonate or bicarbonate in the presence of water, then dipping into the suspension obtained a hollow frame or box, having at one (or more than one) of its sides a filtering membrane or its equivalent, placing the inside of the frame or box under less pressure than the outside, and drawing off from its inside liquid which passes through the membrane, then surrounding with water the frame or box and the calcium carbonate adhering to it, and then continuing to apply reduction of pressure at the inside of the frame or box until the calcium carbonate has been sufficiently freed from ammonium sulphate.

Tchudy (U.S. Ps. 1155385 and 1155386) obtains ammonium sulphates from coal-distillation gases by sulphuric acid.

Coloration of the Ammonium Sulphate.

The article sent out into the trade is hardly ever quite white; it is usually grey or yellow, or red, brown, or blue. Although these colours have no influence upon the function of that salt as a fertilizer, and the substances causing them are only present in extremely slight quantities, such coloured sulphate is frequently objected to. The causes of the coloration are different. According to the *J. Gas Lighting*, etc., 1905, p. 360, if the acid is saturated down to the specific gravity =49° Tw., the salt produced is white, but soon takes a blue colour owing to the formation of Prussian blue; or a yellow colour if the ammoniacal liquor had contained tarry substances, in which case light tar-oils and phenols get into the acid bath. Acid containing iron sometimes causes a red colour of the sulphate through the formation of sulphocyanide.

We shall deal with the causes of the blue colour of ammonium sulphate in a later part of this chapter, when describing the properties of commercial sulphate of ammonia.

When using acid containing arsenic and iron in closed saturators, the salt obtained is more impure than that produced in open saturators, where the froth, forming there, which consists of sulphides and of tarry matter, is regularly skimmed off, whilst in the closed saturators this is not possible. We have mentioned this *supra*, especially also the communication from Mr Watson Smith (p. 1469), describing the way of obtaining perfectly white sulphate. To be sure, as pointed out by Francke, when working in open saturators and taking out the sulphate at once after the acid is neutralized, there is always a loss of ammonia on drying the salt, and the acid sulphate thus formed is not liked in the trade. This is confirmed by Koppers, who points out that such acid sulphate is not fit for being exported, as the acid gradually destroys the bags or casks in which it is sent out. This drawback has been avoided, *e.g.* at Silesian factories, by drying the sulphate at higher temperatures, and grinding it before sending it out; but this proceeding is somewhat expensive. On the other hand, by means of closed, continuously working separators, it is possible to produce at once an almost neutral sulphate of at least 25 per cent. NH_3 (chemically pure $(NH_4)_2SO_4$ contains 25·75 per cent. NH_3), and no more than 0·4 per cent. free acid, as demanded by the conditions laid down by the German Ammonia-selling Union.

Gebrüder Hinselmann (Ger. P. 284641) obtain pure ammonium salts, remaining colourless when kept in stock, from slightly coloured crude salts by heating the crude salts not quite up to the point where they volatilize, whereby the soluble impurities are transformed into insoluble compounds, and can be removed by recrystallizing the salts.

H. Koppers (Ger. P. 254014) treats the ammonium sulphate taken from the saturator, after mechanically removing the mother-liquor, with gaseous ammonia from the main current, whereby the free acid is saturated and the salt is dried.

Dahl (Ger. P. 266192) removes the brown colour produced in ammonium sulphate by iron-thiocyanate compounds, by treatment with a solution of ammonia or of uric acid.

Rigby and Wetcarbonizing, Ltd. (B. P. 18559, 1914), prevent the coloration of ammonium sulphate, caused by tarry particles adhering to the sulphate liquor, by mixing this liquor with light tar-oils, which dissolve the tar adhering to the ammonia, and are separated from the liquor by decantation.

Treatment of the Sulphate taken out of the Saturator.

The crystallized mass taken out of the saturator is first put on to a *draining-bench*, that is an inclined wooden bench, covered with sheet lead, and placed in such manner, that the draining-off liquid runs back into one of the saturators. Sometimes the sulphate is simply taken away from these drainers after a few hours as it is, and sent out into the market.

The sulphate obtained in this way is, however, very incompletely dried and very acid, and rejected by many buyers. It is therefore decidedly preferable to pass it through a *centrifugal machine*, from which it issues with about 4 per cent. water, which during the keeping of the sulphate in stock still partly evaporates, so that it can be sent into the market containing only 2 or 3 per cent. water and about 0·4 per cent. free sulphuric acid.

A centrifugal machine, constructed for this special purpose, is built by Heinrich Koppers, of Essen. It is driven by an engine connected directly with it. The spindle carrying the draining-cylinder is placed in the upper part of a strong cast-iron frame; by avoiding any bearing at the bottom, no liquor can get into the moving parts. The salt is discharged through an opening at the bottom of the cylinder.

During the centrifugalling, the free acid present in the salt can be removed by squirting a small quantity of water on to it, after the mother-liquor has been removed. In lieu of water, Wendriner (Ger. P. appl. W34730) employs a solution of ammonia in this process, thus obtaining a neutral salt of regular composition.

Wilhelm (Ger. P. 286242) employs for draining the ammonium sulphate a semi-cylindrical vessel, mounted on trunnions, so that it can be tilted into the centrifugals.

As the ordinary ammonium sulphate, containing a little water, on being kept in stock for a long time turns into a hard mass which requires grinding, Robert Müller (Ger. P. 223098) submits the sulphate, obtained by centrifugalling and washing with water, to a second centrifugalling under the influence of dry air.

Bonneau and Hasenfratz (Fr. P. 468535) treat crude ammonium salts, after drying and removing the sulphur by means of chloroform, by extracting them in a diffusion battery by means of condensed water, containing NH_3, from the drier. The residue is worked up, with the aid of hot milk-of-lime, into calcium ferrocyanide, which can be precipitated by potassium chloride as a double salt.

R. England (B. P. 10781, 1908) removes the moisture and free sulphuric acid, which damage the packages and may be injurious when employing the sulphate for agricultural purposes, by mixing it with dry, ground phosphates.

The *store-rooms* for the finished salt are preferably protected by covering the floor and the sides with sheet lead, or with asphaltic cement. This is especially necessary when storing the salt, merely drained on benches, not by centrifugals. In that case the lead-covered floor should be slightly inclined to one side, with a shoot for running the draining-off liquid into a lead-coated box. The drying of the salt should be promoted by steam-heated pipes, placed along the sides of the room. Sometimes special, mechanically driven, drying apparatus are employed, like the Thelen pans, described in Lunge's *Sulphuric Acid and Alkali*, 3rd edition, iii., pp. 123 *et seq.* (1911).

The *granulating, drying, and screening* of the ammonium sulphate is effected by the Soc. du Gaz de Paris (Fr. P. 402164), as follows:—The wet salt is fed through a hopper containing a distributing appliance, to the bottom of a chain-elevator, which conveys it into a granulating apparatus. This consists of a series of parallel plates, milled at their edges and mounted on a common vertical axis, about which they rotate horizontally between baffle-knives, fixed to the casing of the apparatus. From here the material gets into a drying-chamber, consisting of a long horizontal cylinder, fitted with a screw-conveyer. Hot gases pass from a furnace through the cylinder in the opposite direction to that of the material. Near the extremity of the drying-chamber, the dry salt falls through a screen into a delivering hopper; any material which is too coarse to pass through the screen is propelled by the conveyer against a grooved plate, which forms the end wall of the drying-chamber. The material thus lodged between the end of the conveyer and the grooved plate is thereby subjected to a process of trituration, which enables it to pass through the screen.

Packages.—In Germany the sulphate of ammonia is usually sent out in bulk in closed railway trucks. In Great Britain, however, and everywhere for the export trade, it is packed in bags, holding about 2 cwt. each.

PREVENTION OF NUISANCE FROM AMMONIA-WORKS.

Ammonia-works, if not quite properly constructed, may be a great nuisance to the neighbourhood. The sources of this are various, and will be dealt with *seriatim.*

1. *The Reception, Transportation, and Storage of the Ammoniacal Liquor.*

These operations can be made innocuous wherever the sulphate-works are within reasonable distance of the gas-works which produce the ammoniacal liquor, by conveying it by means of pipes. Dr Ballard recommends underground pipes; but we should decidedly prefer overground pipes, wherever possible, as in the former leakages may occur and continue for a long time without being detected. Wherever the liquor has to be conveyed to a greater distance, tank-wagons or barges are employed, exactly like those used for conveying gas-tar, and similar precautions should be taken in both cases. Pipes should be laid from the gas-works to the place of loading; the tank or hold of the boat should not be covered with loose planks in the perfunctory way often noticeable, but closely; the tar or liquor should be introduced by a close conduit, and, to prevent all nuisance, provision should be made for the escape of air from the tank through a box, containing trays charged with hydrated iron peroxide. Tank-wagons should be charged from elevated reservoirs by a hose, through a manhole at the top, without exposure to the air; the manhole is afterwards closed by a tightly screwed-down lid. On arriving at the sulphate-of-ammonia works, the liquor should be run or pumped into the reservoirs with similar precautions, the vent through which the air must escape being guarded by a small oxide-of-iron purifier.

2. *Leakages about the Apparatus.*

These may cause local escapes of foul gases. This may, for instance, occur about the angles or edges of the curtain in fishing-boxes, by lids not being properly fastened down, by insufficiently luting the curtain with liquor, etc. Nuisance arising from such cases can be instantaneously detected by those in charge of the works, and may be prevented by ordinary care.

3. *Treatment of the Condensed Water.*

The gases escaping from the saturator, consisting principally of CO_2 and H_2S, carry very much steam along, which must be condensed by cooling before dealing with them by combustion, etc. (see p. 1497). The condensed water is, on account of its extremely objectionable smell, called "devil's water," and is not very easy to deal with. If mixed with the lime-mud, it renders the latter all the worse to remove. Allowing it to drain away in the soil is not always practicable. Some run it into the ash-pit of the gas-retorts. The best method is to run it back into the stills; but this causes waste of fuel. Where the sulphuretted hydrogen is removed by oxide-of-iron purifiers, the "devil's water" can be filtered through the spent oxide. This can be avoided by taking away the water at the hottest part of the condensing-apparatus, where it contains so little H_2S that it may be run away without any trouble; but then the gases are not very well dried and are more difficult to treat.

4. *Waste Liquor and Lime-mud from the Stills.*

Usually these waste liquors are discharged while hot, and the slight proportion of ammonia they contain is then given off, and causes a very perceptible smell in the neighbourhood. The obvious remedy is, to thoroughly exhaust the liquors.

Lubberger[1] estimates the ammonia in waste still-liquor as follows:—Into a round-bottomed flask, holding 400 c.c., three lumps of quicklime of the size of a walnut are placed, the flask is half-filled with liquor, hot from the still, a cork is inserted, and the whole shaken up, until it takes a dark brown colour. When the lime has been slaked, the flask is cooled under a water-tap, 50 c.c. is filtered into a beaker, and titrated with seminormal hydrochloric acid until the brown colour suddenly changes to light yellow. From the acid employed, the quantity required by the dissolved lime is deducted; the remainder has been used for combining with ammonia.

Dr Ballard mentions that Mr Steuart, of Clayton, reduced the ammonia in the liquor down to 0·002 per cent. The hot waste from the still should not be conveyed away by an open channel, but by a pipe. Before reaching a common sewer or public watercourse, it must necessarily pass through a settling-tank, both in order to separate the solid refuse from the liquor, and to completely cool the latter before it gets into any sewer with which house-drains communicate, or into any watercourse in which fish exist. The settling tank should be covered over, and should be ventilated merely by a pipe of sufficient length to condense any vapours rising through it. The lime deposit (which contains a great deal of calcium sulphide) should never on any account get into the sewers or watercourses, where it is sure to give off sulphuretted hydrogen. Even where it is entirely kept back in the settling-tank, it may cause nuisance when being disturbed for removal, and again when depositing it on a heap. It should therefore be removed as expeditiously as possible, and with all imaginable precautions against unnecessary exposure to the air. It should be covered up during transmission from the premises, and if shot down in any open place where it is likely to be a nuisance, the surface of the heap should at once be covered with earth and patted down. Wherever that is not possible, it is best to excavate large pits in the ground, which, after being nearly filled with such lime waste, are covered up with soil again. But in this case care must be taken that no nuisance arises by foul drainage from such pits.

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[1] *Z. angew. Chem.*, 1899, p. 109.

In some cases the lime waste may be utilized by grinding it up with a little fresh lime and a good deal of cinders or the like, when it will form a very well-setting and somewhat hydraulic mortar, which approaches in composition the well-known Scott's cement.

Even when the waste liquors have been completely clarified by repose, and have been practically freed from ammonia, the neighbours or the public authorities often oppose their discharge into public watercourses, on account of the tarry matters, which impart to them a brown colour and a certain smell. Such opposition is sometimes founded on quite unreasonable grounds, *e.g.* on the presence of calcium chloride, which, of course, is both unavoidable and harmless; but the same cannot be said of the tarry matters, etc. Sometimes, owing to the presence of such matters, the liquors will not even readily clarify. In such cases a remedy, as I have convinced myself by experiment, is nearly always possible by producing in the liquor a precipitate of hydrated oxide of alumina or iron, which carries down the tarry matters and other impurities, and leaves a nearly colourless and quite inoffensive liquid. Such a precipitate is caused by adding a sufficient quantity of sulphate of alumina, or preferably, of sulphate or chloride of iron, along with sufficient lime to completely precipitate the metallic base, but no more.

König[1] found in waste liquor from ammonia-stills 20·453 g. solid residue per litre, containing:—

Calcium sulphocyanide	2·328
Calcium sulphide	2·563
Calcium thiosulphate	1·091
Calcium sulphate	0·578
Phenols, etc., extracted by ether . . .	0·608
Lime	6·448
Other matters, partly combined with lime	6·805

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[1] *Verunreinigung der Gewässer*, Berlin, 1887, p. 354.

(Evidently this liquor had not been clarified.) The deleterious effect of such liquor is usually ascribed principally to the sulphocyanide (thiocyanate), although this is not quite certain. Where the sulphocyanide is recovered from it (cf. *infra*), probably no nuisance will result from this quarter, except where the spent liquors are submitted to the "bacterial" treatment, since phenols are poisons for the bacteria. P. F. Frankland and H. Silvester (*J. Soc. Chem. Ind.*, 1907, p. 231) found that the average contents of the spent liquors examined by them was 153·8 parts of sulphocyanide (in maximo 171·7 parts) per 100,000, the average contents of the sewage containing such liquors being 9·3 parts in 100,000. Gold-fish can live at least twenty-four hours in solutions containing up to 250 parts CNS per 100,000; at 450 parts they showed signs of distress; at 500 parts they died. But bacteria are much more sensitive; *Bacillus coli communis* suffers already in the presence of 10 parts CNS in 100,000. The sulphocyanide is not destroyed by the septic treatment.

Skirrow (*J. Soc. Chem. Ind.*, 1908, p. 58) estimates the amount of phenols lost in the spent ammonia liquors at 0·37 to 0·55 lb. per ton of coal carbonized, against 0·53 lb. recovered in the tar, so that about half of the phenols produced in the gas-retorts is lost in the spent liquor. He estimates the quantities of substances, contained in these liquors, per 1000 c.c. of effluent, expressed as sodium salts, at :—

Tar acids . . .	2·12 grams.
Sodium thiocyanate . .	3·14 „
Sodium thiosulphate . .	1·58 „
Sodium ferrocyanide . .	0·28 „

Bacterial Treatment of the Liquor.—Lowe and Ely (B. P. 19074, 1910) filter the waste ammoniacal liquor through coke, then mix it with animal charcoal, and pass it into a settling-tank, where bacterial action takes place, with the result that the animal charcoal absorbs any free ammonia present, as well as the whole of the tar-oils and the phenoloid bodies. At the outlet of the settling-tank the effluent is pure enough to allow of its being discharged into rivers or streams.

G. J. Fowler (*Forty-fourth Report of the Alkali Inspectors*, p. 51) found that the bacteria oxidize the thiocyanate to sulphate, and also destroy the phenols. The spent liquor absorbs 250 grains oxygen per gallon; the effluent afterwards on the average only 22 grains. This process is also discussed in the ninth report of the Royal Commission on Sewage (quoted in *Chem. Trade J.*, 1915, p. 374). The Bradford Corporation are now treating the whole of the waste liquor from the Corporation gas-works in this way, and thus obtain a purification of over 80 per cent., as measured by the oxygen absorbed from permanganate in three minutes. The inventor had come to the conclusion that it is better to allow a dilute solution of the liquor to circulate again and again through the filter, rather than to pass a very highly diluted liquor through once.

Diamond (B. P. 15543, of 1899) clarifies the spent liquor, after settling out the mud in the ordinary way, by means of alumino-ferric cake, which is afterwards removed by means of a filter-press.

Recovery of Sulphocyanide (Thiocyanate) and Ferrocyanide from the Waste Liquor.—We have previously (pp. 1450 *et seq.*) described Grossmann's process for working-up ammoniacal liquor without the formation of a noxious effluent and with recovery of sulphocyanides and ferrocyanides. Later on (*J. Soc. Chem. Ind.*, 1908, p. 394; B. P. 7932, of 1907) Grossmann again treats the question of dealing with the effluent, particularly in view of his new process for treating the crude gas-liquor for the extraction of cyanides before distillation. The simplest method is to run that effluent into disused pits, but these are available only in special localities, and even there it might find its way into courses used for domestic water. The evaporation of these liquors to dryness is too costly; their use for coal-washing or coke-quenching also leads to trouble. The attempt at using them in steam-boilers has hitherto failed, principally owing to the formation of thick scales of calcium sulphate, but not, as formerly assumed, through a corrosive action of the sulphocyanide upon the iron, which action, as found by Grossmann, is not serious even at a pressure of 40 to 50 lb. per square inch. His own process for dealing with the effluent consists in removing the sulphates by means of barium carbonate, according to the reaction:

$$CaSO_4 + BaCO_3 = CaCO_3 + BaSO_4.$$

This reaction does not take place at once, even on shaking for a considerable time, but after settling for eight or ten hours the clear liquor is absolutely free from sulphates. For practical reasons one should employ an excess of barium carbonate which is not lost, if the settlings are used for a second operation, adding only as much barium carbonate as had been decomposed. Only after a good many, say twenty, operations the bulk of the precipitate will compel its removal, and even then there is no loss, since by levigation the barium sulphate can be separated from the calcium carbonate, and its value will pay for the barium carbonate lost.

The agitation with barium carbonate may be performed in a continuous washer; the liquid is passed through settling-tanks, and after about twelve hours it is clear enough for use in the steam-boilers. Of course the solids dissolved in it will accumulate in the boilers, and after a certain time a certain quantity of the liquid will have to be blown off every day. These blow-offs, as well as the final blow-off at the time of boiler-cleaning, may be treated for the recovery of thiosulphate or evaporated to dryness in a special furnace, which is now feasible; as its bulk is only one-tenth or even less of the original volume.

Grossmann estimates the cost of this process for eliminating the sulphates from the effluents to ¼d. to ½d. per ton of coal carbonized.

J. Radcliffe (B. P. 10075, of 1905) recovers the sulphocyanide from the spent liquor and at the same time makes this innocuous by the following treatment:—The neutralized (or slightly acid) liquor is run into a tank, together with a regulated quantity of copper salt solution, in a continuous manner. If the copper salt is in the cupric state, sufficient sulphurous acid must be added to effect its reduction to the cuprous state. The precipitate of cuprous thiocyanate formed is separated by filter-pressing, and by means of alkali it is converted into Cu_2O and marketable cyanogen compounds. Any copper present in the filtered liquor is removed by precipitation, either by means of lime or an alkali, or of metallic iron, and is then discharged in an innocuous state. It has a beneficial effect when added in the "bacterial treatment" of sewage.

Bower (B. P. 2918, of 1882) recovers from the waste still-liquor *ferrocyanide*, by neutralizing it with acid and thus precipitating Prussian blue. (*Cf.* Grossmann's process, *supra*, p. 1494.)

Knoedler (*J. Ind. Eng. Chem.*, 1915, pp. 1061 *et seq.*) describes the recovery of ammonia from waste liquor at the works of the Welsbach Co., Gloucester, N.J., U.S.A.

5. *Gases and Vapours given off in the Saturator.*

The gases escaping from the saturator consist of carbon dioxide, sulphuretted hydrogen, sometimes a little hydrocyanic acid, a small but very perceptible quantity of hydrocarbons, and perhaps also of sulphuretted organic compounds; all of them mixed with a large quantity of steam.

If this gaseous mixture were allowed to escape freely into the atmosphere, the nuisance would be altogether intolerable. It is bad enough if only a small proportion of it finds its way outside the works; even then the smell may be perceived at a distance of half a mile or more. Nor can the offenders easily evade detection; the smell of these gases is easily recognizable by its peculiarity. The public have a special dread of it, and thus any escape of this kind is sure to be soon traced to its origin and is fruitful of complaints.

Dr Ballard (*Report of the Medical Officer to the Local Government Board* for 1878, p. 131) expresses himself as follows about this matter:—"Medical men are usually ready to certify that the effluvia are injurious to public health, probably referring to the effects produced on those who are exposed to their influence in a diluted form, to the operation of the sulphuretted hydrogen as a poison. The public also readily believe that an atmosphere even slightly thus contaminated is dangerous to live in. It is certain that exposure to the diluted effluvia from sulphate-of-ammonia works does in many persons induce feelings of depression, headache, loss of appetite, nausea, or vomiting, and sometimes some oppression of the breathing."

These gases and vapours are the chief source of complaints of nuisance from ammonia works, and from this cause (as well as on account of the waste effluents) legal proceedings have been several times taken.

In some cases it seems sufficient to discharge these gases, etc., from the separator into a tall *chimney-shaft.* Especially where they can be first brought into communication with hot furnace-gases, this seems to suffice for removing the nuisance, as is proved by some works in Manchester, where shafts, 180 and 196 ft. high, serve for this purpose. Where the liquor is worked up at the gas-works themselves, there is never any difficulty of that kind, as the immense volume of highly heated gases coming from the retort-fires is far more than sufficient to burn and dilute all effluvia from the ammonia-plant.

According to a communication from Mr Heuss, many German coke-works pass the gases from the saturators directly into the pipe by which the gases are aspirated from the coke-ovens, so that they are ultimately burned in these, and the products of combustion are removed by the chimney.

Combustion of the Saturator-gases.—In cases where there is no very tall chimney-shaft, or even with a tall shaft but an unfavourable conformation of the country, a thorough *combustion* of the gases must be aimed at. This is ordinarily done by carrying them by a pipe from the saturator into the side of the boiler fire, or under the fire-grate, or sometimes into a fire specially kept up for this purpose. But unless care is taken to previously remove the large quantity of aqueous vapour contained in the gases, the object in view will be only partially attained, or even quite frustrated by the vapours extinguishing the fire. It should therefore never be neglected to provide means for condensing the aqueous vapour. At some works the pipe which conveys the gases is continued into a worm, placed in a tank filled with gas-liquor or with water for feeding the steam-boilers, which are thus heated up previous to use. At the Plymouth gas-works an 8-in. pipe from the saturator is first carried beneath the floor on which the sulphate is dried, and thence runs along the surface of the ground, where it is bent upon itself, for a distance of about 500 ft., in the course of 290 ft. of which it is played upon by jets of water flowing from a perforated pipe above it. At the Stampshaw works the 8-in. pipe from the saturator is first carried round the outside of the building at the eaves, and then enters a worm-condenser. At Illingworth's works at Bradford special care is taken to remove the aqueous and any other condensable vapours, because the sulphuretted hydrogen is there utilized for the manufacture of sulphuric acid. The gases are first conducted into a chamber made of an old boiler, through which passes the pipe conveying the liquor to the Coffey still, and they thus serve to heat up the liquor; then by a pipe to two iron towers, divided by partitions springing at opposite sides alternately in such a way as to make a tortuous passage for the vapour; and, lastly, from these towers through a long series of vertical iron pipes, bent upon themselves in the same manner as a continuous condenser, such as is used in gas-works, water being made to flow continually down the outside of the pipes from a perforated water-pipe above. Other means for cooling the gases, and condensing the aqueous vapour therefrom, will be mentioned when describing in detail some of the varieties of plant seen by myself.

The condensed liquid, if not quite cold, may by itself cause a nuisance, and should therefore be cooled down before discharging it into a public drain.

The *combustion of the dried gases* is usually carried out by making them pass through a small coke-fire; and the sulphur dioxide, produced by the combustion of the sulphuretted hydrogen, is usually discharged with the fire-gases up the chimney, and thus thrown away. Sometimes the gases are burned by themselves, *e.g.* at Messrs Forbes & Abbott's works at Old Ford, where they enter by a 1-ft. square opening into a small firebrick chamber and thence into a firebrick flue about 15 ft. long, 2 ft. 6 in. wide, and 3 ft. high; air is supplied by a small circular hole in an iron plate near the entrance of the gas, and the gases are ignited. Once the chamber and flue are red-hot, there is no fear of the gas being accidentally extinguished without relighting. The heat thus generated is then utilized for heating steam-boilers, which are stated to have lasted for fourteen years, without receiving any injury by corrosion from the acid gases. The products of combustion, containing a large proportion of sulphur dioxide, are sent up the chimney-shaft.

Chateau[1] describes the apparatus used at Arcueil for deodorizing the gases evolved in the manufacture of sulphate of ammonia. They are aspirated by a fan-blast through a coke-column, 17 ft. high, in which is spread a mixture of ferric oxide and calcium sulphate, constantly moistened by a solution of ferrous sulphate. Here ammonia and carbonic acid are retained [hardly completely!]. The gases on issuing from the fan-blast pass over a thin layer of camphor and then into a combustion-furnace constructed by M. Perret. The grate-bars of this furnace are only $\frac{1}{24}$ in. apart, and are so deep that they can be made to dip into a water-basin in order to cool them and retain their shape. The gas enters in the narrow space between the water-basin and the grate. The latter is charged with anthracite dust, which is partly carried away by the gaseous current, but it is completely burnt in zigzag flues, made of fireclay flags, which soon attain a white-heat. At this high temperature hydrogen sulphide, ammonium sulphide, cyanogen compounds, and any other deleterious gases are completely burned, air being admitted by special openings for this purpose. The strong heat generated is employed for heating a steam-boiler. This apparatus is in regular operation, and is said to give very satisfactory results.

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[1] *Bull. Soc. Chim.*, xxvi., p. 195.

It should not be overlooked that the sulphur dioxide thus formed and discharged from a chimney may itself become a nuisance—no doubt much less than that which the sulphuretted hydrogen would have produced, but still sufficient to give rise to complaints. Besides this it may sometimes happen that the sulphuretted hydrogen is but imperfectly burned, and that enough of it escapes to create a nuisance.

All this can be overcome by one of two ways—either absorbing the sulphuretted hydrogen by some means, or burning it and *utilizing the* SO_2 *to produce sulphuric acid.* The latter process has been in practical operation for several years past, first at Mr Illingworth's works at Frizinghall, near Bradford, then at Messrs Spence's works at Birmingham, and probably elsewhere. The gas is burned in a firebrick chamber 12 ft. long, 3 ft. deep, and 4½ ft. wide, into which at one end the gas (previously carefully dried) is admitted by a pipe. There is a small air-opening close by. The products of combustion must pass through several pigeon-holed walls built across the chamber, in order to mix the gases and make the combustion perfect. They then play round the usual nitre-pots, and the mixture of SO_2, steam, nitrous fumes, nitrogen, CO_2, surplus air, etc., is carried into ordinary vitriol-chambers. If the combustion-chamber is once properly heated, the gas keeps lighted and the combustion proceeds satisfactorily; when the work is stopped, for instance on Sundays, the heat of the chamber is maintained by a small coke-fire, burning on a grate just below the entrance of the gas-pipe.

It cannot be doubted that this process is entirely successful in removing all nuisances; but the presence of carbon dioxide, etc., in the gases sent into the vitriol-chambers, is very injurious to the acid-forming process, and it seems doubtful whether there is, under ordinary circumstances, much profit to be made out of it. But the process must be considered to have answered its purpose if it effects the removal of the nuisance from the waste gases, even without any profit accruing from this.

Claus Process.—A much more profitable process than burning sulphuretted hydrogen for the manufacture of sulphuric acid is that of burning only the hydrogen and obtaining the *sulphur in the free state.* The best known process of this kind is that of C. F. Claus (B. Ps. 3606, of 1882; 5070 and 5958, of 1883), which, in connection with its application to the recovery of sulphur from the "tank-waste" of Leblanc alkali-works, has been thoroughly worked out, especially by Messrs Chance, of Oldbury. A complete description of this process is given in Lunge's *Sulphuric Acid and Alkali*, 3rd ed. (1909), ii., pp. 945 *et seq.*, to which we must refer the reader for all details; we only mention that it consists in mixing the gas containing sulphuretted hydrogen with a quantity of air containing as nearly as possible the proper quantity of oxygen to produce the reaction $H_2S + O = H_2O + S$, and passing this mixture through a "Claus kiln," that is, a large iron cylinder lined with firebricks and partially filled with red-hot oxide of iron (pyrites-cinders), which acts as a "catalytic substance." The issuing mixture of sulphur vapour, steam, nitrogen, and some undecomposed sulphuretted hydrogen is cooled down to recover the sulphur in the liquid or solid form, and the gases are ultimately passed through a purifier before issuing into the atmosphere. A Claus kiln of 25 ft. diameter produces from 15 to 20 tons sulphur in six days; about 85 per cent. of the sulphur is recovered, partly as block sulphur, partly as "flowers."

We shall now describe a Claus plant specially erected for gas-works, at Leicester,[1] and serving for a weekly production of 35 or 40 tons sulphate of ammonia. The dried gases from the saturator (whose heat has been utilized for heating-up fresh gas-liquor) are conducted by a 6-in. pipe, *a* (Fig. 331), into the kiln A. This consists of an iron shell, with 18-in. brick lining, 3 ft. wide and 5 ft. long inside. A perforated partition, *c*, causes an intimate mixture of the gas and the air entering at *a* and *b*. The inner chamber, with an area of 3 ft. × 3 ft., is filled with lumps of oxide of iron, containing a little manganese, 1 to 1½ in. diameter. The sulphur generated here is deposited in chamber B, divided in the manner shown in the plan. From B the residual gases traverse a flue, E, 2 ft. 6 in. wide and 58 yards long, in which are inserted a number of baffle walls, to within 12 in. of the bottom of the flue. At the end of flue E, which is in the form of a hollow square, the scrubber C is attached, 24 ft. high and 4 ft. diameter, packed with limestone over which water is flowing; here sulphuric acid, and probably also some sulphuretted hydrogen, are arrested, the remaining H_2S passing on to the open oxide-of-iron purifier D, 12 ft. 10 in. square. On the bottom grids of

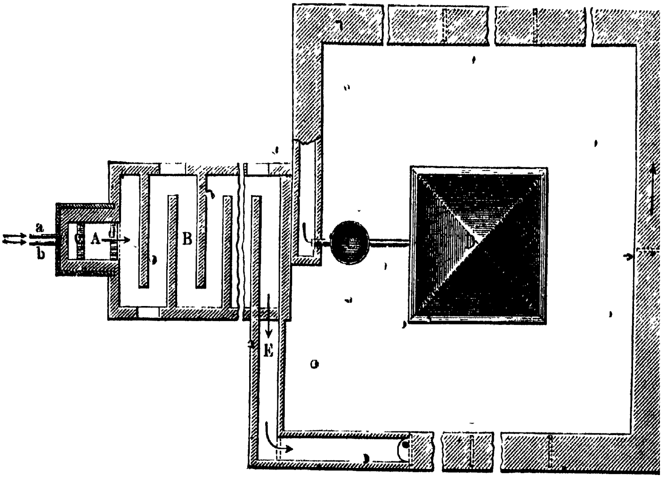

FIG. 331.

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[1] *Alkali Report*, No. 23, p. 81.

this, coke is placed to retain any moisture that may have remained in the gases; on the second grids oxide of iron to the depth of 3 ft. 6 in.; the CO_2, now freed from sulphur compounds, passes away into the air. The apparatus C and D are decidedly necessary, as without them the gases from Claus kilns show acidities up to 12 g. SO_3 per cubic foot (*Alkali Report*, No. 23, p. 71).

In the *Thirty-sixth Alkali Report*, pp. 181 *et seq.*, experiments are described to adapt the Claus sulphur recovery method to the Scotch conditions by supplying a heat-retaining jacket to the kiln, in order to promote the reaction, or at least to prevent loss of heat by radiation. Large-scale experiments of the same class are described in the *Thirty-eighth Report*, pp. 148 *et seq.*, and it would seem that this modification answers very well for the treatment of dilute gases.

Van Eyndhoven (Ger. P. 170554) interposes between the saturator and the Claus kiln, first, a cooler for the condensation of steam into water; secondly, a cyanide washer.

Carpenter and Claus (*J. Soc. Chem. Ind.*, 1904, pp. 577 *et seq.*) have made an extended investigation of the reactions in the Claus process. Apart from the well-known reactions:

$$(a)\quad 3S + 2H_2O = 2H_2S + SO_2$$

and

$$(b)\quad H_2S + O = H_2O + S,$$

others may occur which explain the facts even better in a thermochemical direction, viz.,

$$(c)\quad 3H_2S + 3O = 2H_2S + SO_2 + H_2O$$

and

$$(d)\quad 2H_2S + SO_2 = 3S + 2H_2O.$$

On the foundation of many experiments, also on the large scale, observations at factories, and calculations, the authors tried to fix the conditions prevailing in Claus kilns, the conditions influencing the yield of sulphur and the part played in the process by ammonia. Ammonium sulphide is never found, but sometimes sulphite and sulphate, as well as thiosulphate and polythionates. Some samples of recovered sulphur contain so much ammonia that it must be removed by washing before burning the sulphur for the manufacture of vitriol. Hydrocyanic acid greatly reduces the yield of sulphur; NH_3 is formed from it by the reaction:

$$HCN + H_2O = NH_3 + CO.$$

Where the output is too small to make the Claus process available, and the disposal of the gases to a vitriol plant is impossible, the treatment by combustion and *absorption by calcium carbonate* is sometimes adopted with great success (*Thirty-fourth Report of the Alkali Inspectors*, pp. 29, 114, 115; *Thirty-fifth Report*, pp. 117, 118; *Thirty-sixth Report*, pp. 25, 79, 153). The gases, after being subjected to thorough cooling, in order to remove aqueous vapour, pass to a furnace designed especially to act as an accumulator of heat, where complete combustion of the H_2S to SO_2 is effected. With gases containing 20 per cent. by volume of H_2S, the flame of a large gas or jet is sufficient to initiate and maintain combustion at the end of the pipe bringing the foul gases to the furnace, the reaction being made complete by prolonged travel of the gases over the surface of brick and tiles kept at a bright red-heat. Provision is made for supplementary air being admitted at various points in the furnace, so that no vapour of sulphur may pass unoxidized. Attention to this point is of the first importance; otherwise sulphur is deposited in the solid state in the later portions of the apparatus, and the disorganization, once commenced, rapidly increases, as the primary supply of air is checked by the diminution of draught at the furnace. The gases, after subsequent cooling to air temperature, pass to the bottom of a tower packed with limestone and fed on the top with a shower of water, *e.g.*, by the arrangement used for Gay-Lussac towers, in the condensation of hydrochloric acid, etc. (Lunge's *Sulphuric Acid and Alkali*, 4th ed. (1913), i., p. 799). Under these conditions the SO_2 is fixed by the CaO of the limestone, and issues from the bottom of the tower in solution as calcium bisulphite.

At one of the Metropolitan works the limestone scrubber consists of a wooden structure made of 1½-in. tongued and grooved boards, 5 ft. 6 in. square and 21 ft. high. Layers of Derbyshire limestone in good-sized pieces are supported on stout wooden gratings, the layers of stone being some 9 in. deep. Manholes for recharging the trays with fresh stone, as this wastes away, are provided above each tray. A tumbling-box for flushing with water is fixed inside the scrubber at the top, at which point the neutralized gases leave the apparatus for the draughting chimney. The inlet and outlet pipes are of cast-iron, but lead would perhaps be preferable, as there is some little action of the gas on the iron. The average acidity of the gases on entering the scrubber at that works is 41·40 grains SO_3 per cubic foot, on leaving the scrubber 0·81 grain, showing a condensation of 98·05 per cent. On the average of all the works the condensation may be put=95 per cent.

After several years' experience of this process, the Alkali Inspectors state the following precautions to be absolutely necessary for success:—

1st. There must be command of draught at the furnace, *i.e.*, the suction at the condenser outlet must be adequate to supply this at all times, else sublimation of sulphur with attendant evils will occur. Possibly air might be supplied to the furnace under slight pressure, equal to that of gases from the saturator.

2nd. Adequate and complete cooling of the gases before the furnace and also afterwards. If the gases enter the limestone tower above 38° C., containing as they will an excess of oxygen with sulphur dioxide, the formation of $CaSO_4$ is promoted. This forms a protective crust on the surface of the limestone, thus impeding the action of the latter on the SO_2. The condensation of water from a hot gaseous mixture, containing steam $+SO_2$, causes great corrosion of the iron pipes, especially at the chaplets of the pipes, which are of wrought-iron. Here lead should be used for the pipes, ensuring the delivery of the gas at the tower at a temperature not above 38° C., or lower if possible.

3rd. Cast-iron does not seem the best material for use in the construction of the tower. Wood planks tongued and grooved last well, even in summer heat, and cement towers have stood well.

4th. The supply of water is best arranged in two forms, one constant, the other intermittent (by flushes), at least in the case of limestone which is not a porous body, and holds no reserve of condensing power within itself like coke. But if hard chalk is used, the intermittent flush, at no great intervals, is admissible.

Wilton (Manager of the Beckton Tar and Ammonia Works) in his B. P. 15468, of 1901, describes a process whereby the H_2S is burned in a suitable furnace *with an excess of oxygen.* The hot mixture of SO_2, free O, N, etc., is passed through iron scrap, contained in towers fed with water or mother-liquor from the sulphate of iron crystallizing tanks. Thus a concentrated solution of sulphate of iron is produced, which is allowed to crystallize in suitable vessels. Or else the towers are packed with limestone, in which case a solution of calcium sulphate is formed, which may be run to waste as a practically inoffensive fluid, and such a limestone tower may be placed behind the scrap-iron towers, in order to catch the SO_2 escaping from these.

Becker (Ger. P. 278776) destroys the noxious gases and vapours, formed in the distillation of ammoniacal liquor, as well as the very badly smelling condensing-water, together with the recovery of sulphur, by burning these gases in well-known manner (preferably by the assistance of catalytic agents) so as to convert the hydrogen sulphide into sulphur dioxide, and bringing this into contact with the condensing-water, *e.g.* in a column fed with this water. According to his Ger. P. 282873, only part of the gases is burnt, so as to convert the H_2S into SO_2; the gaseous mixture is then brought into mutual action in a reaction-tower, the upper part of which serves as a cooler, and the sulphur produced retained in a washer.

According to Reinhardt (*J. Gasbeleucht.*, 1915, lviii., p. 64) the disagreeably smelling waste gases formed in the manufacture of ammonium sulphate, and consisting essentially of CO_2 and H_2S, are almost entirely deodorised by passing them over wood-charcoal. This is placed in two perpendicular pipes, 14 ft. high and 14 in. wide, filled with about 1½ cwt. of wood-charcoal each. After six weeks this is taken out and regenerated by three hours' heating in a gas-retort. The necessary draught is produced by means of a steam-jet blast in the exit pipe coming out of the roof.

Hemingway (B. P. 9432, of 1899; *J. Gas Lighting*, 1904, lvi., p. 18) removes the H_2S from the ammonium-sulphate saturator gases by a special process with recovery of the sulphur. Ammonium sulphite is produced by saturating ammonia with SO_2, obtained by roasting pyrites or spent gas-purifying oxide; the solution of $(NH_4)_2SO_3$ is made to act upon ferrous sulphate, which precipitates ferrous sulphite, finely suspended in the solution. This suspension is used for washing the saturator gases in two scrubbers, where the following reactions take place:

$$(a)\quad FeSO_3 + 3H_2S = FeS + 3S + 3H_2O$$

after passing in SO_2:

$$(b)\quad 2FeS + 3SO_2 = 2FeS_2O_3 + S$$

after changing the current in the scrubbers:

$$(c)\quad 2FeS_2O_3 + 6H_2S = 2FeS + 8S + 6H_2O.$$

Hence in one of the scrubbers ferrous sulphite is transformed into thiosulphate, while in the other scrubber at the same time ferrous thiosulphate is reduced by hydrogen sulphide into ferrous sulphide; by reversing the current in the scrubbers, the opposite process is made to go on. The final products are free sulphur, ferrous sulphide, and a little ammonium sulphite. The sulphur thus produced is free from arsenic, and its value nearly covers the cost of the process, the principal object of which is the prevention of nuisance.

Becker (Ger. P. 196015) removes the H_2S and HCN from the gases escaping from the saturators by washing them with water and adding this to the waste liquor, which contains free lime and thus saturates the H_2S and HCN.

Feld (Ger. P. 192533) absorbs H_2S from gases by means of metallic compounds, *e.g.* oxides of manganese, which yield insoluble sulphides. These are afterwards heated with solutions of ammonium salts, whereby the metallic compounds are regenerated and the H_2S and NH_3 are expelled.

J. W. Lobb (U.S. P. 1108705) treats gases with a metallic sulphate, capable of forming from H_2S and NH_3 a metallic sulphide and ammonium sulphate. The metallic sulphide formed is treated with air and SO_2, in order to regenerate the sulphate.

Recovery of Pyridine from the Saturator-gases.—Lessing and

Wilton (B. P. 4766, of 1905) recover pyridine bases from the waste gases (or from crude gas-liquor) by washing them with heavy tar-oils, suitably with addition of crude phenols (*cf.* p. 900).

The sulphuretted hydrogen contained in the saturator-gases is frequently, especially at smaller works, *absorbed in a purifier, charged with lime or oxide of iron.* For this purpose the condensable vapours must be equally removed by cooling; and the dried gases are then passed into purifying-apparatus, constructed exactly like those used at the gas-works, and for the same purpose, as shown in Fig. 332. They are cast-iron boxes, provided with a rim at the top for a hydraulic lute, into which dips the flange of the cover. The gases enter at the bottom and pass through trays, usually made of wood on which the purifying-material is spread out in a layer of 3 or 4 in. The purified gas finds its way out through a pipe from the upper portion of the box. Several such boxes are usually combined, so that they can be worked in regular rotation; that box receiving the fresh gases which has been the longest time at work, and that receiving the gases just before escaping into the atmosphere which has been last charged with fresh material. Such boxes are made, for example, from 10 to 20 ft. square and

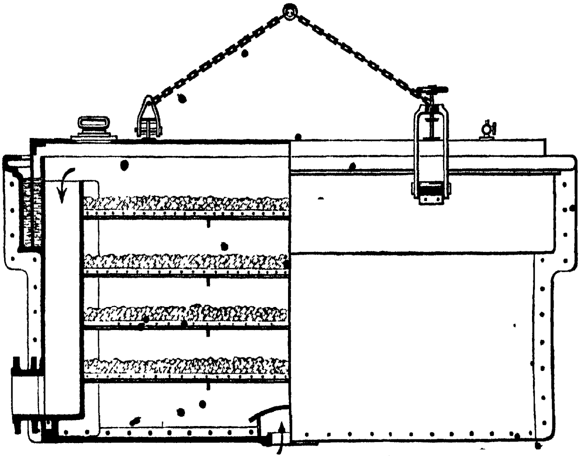

FIG. 332.

from 2 to 4 ft. high; they may also be made of brickwork, but they should not be made of wood, as it is difficult to keep them tight in that case. Moreover, the heat developed in the absorption of H_2S may injure the wood, and for this reason it is also preferable to substitute perforated iron or wire-gauze trays for those made of wood.

Sometimes the absorbing-material used is lime; but this is anything but rational. The lime is wasted in the first use, and the spent lime ("blue-billy") is a fresh nuisance, which may cause considerable trouble. A much better material is that used at nearly all gas-works, namely, the hydrated peroxide of iron, generally mixed with sawdust. This material, when it has ceased to be active, can be regenerated by simple exposure to the air, which causes the iron sulphide to be converted into a mixture of ferric hydrate and free sulphur; and when the sulphur has accumulated to such an extent that the material becomes definitively useless for absorbing H_2S, the "spent oxide of iron" is a valuable material for the production of sulphuric acid, so that its sulphur is turned to a useful purpose.

Sometimes a fan-blast or an injector of some kind is used for driving the gases through the purifiers. In other cases they are connected with a high chimney; but this may cause the purifiers to be left unnoticed for some time, which cannot happen with open purifiers.

If on reviving the oxide, ferrous sulphate is formed, a sufficient quantity of lime must be added to decompose this.

This process is best adapted for small works, up to 300 tons production per annum. At larger works the space required by the purifiers and the labour of reviving the oxide cause great inconvenience.

For this purpose the gases must be deprived of most of their steam, as well as when burning, since otherwise the oxide becomes too dense and does not allow the gases to pass (*cf.* the contrivances described *supra*). A partial cooling of the gases can be produced by blowing cold air into them by means of an injector; this air afterwards assists in oxidizing the sulphide in the purifiers, so that these work continuously. Otherwise the purifiers are worked intermittently, by passing through alternately gas and air, making the change every three or six hours. Care must be taken to keep the valves in good order, so as to protect the men employed for turning over the oxide in the purifiers during the blowing in of air, against the entrance of foul gas intended for another purifier.

The *Alkali Inspectors' Report*, No. 32, p. 16, gives the following analyses of spent oxide—(*a*) from intermittent, (*b*) from continuous work:—

	a	*b*
Water	4·65	24·90
Free sulphur (calc. for dry mass)	73·90	59·80
Sulphur as soluble sulphates	1·00	0·95
Sulphur as insoluble sulphates	traces	0·40
„ „ FeS	1·20	1·85
	80·75	87·90

Many other analyses are given in *Report* No. 33, pp. 16 and 17.

According to *Report* No. 42, p. 23, the opinion of practical men is generally in favour of applying the oxide of iron in the form of a conical heap on a concrete floor, the foul gases being introduced below by a simple gas-distributing device—rather than in that of a specially constructed purifier with retaining walls. The occurrence of fouling in the mass is more easily detected and rectified, and there is less labour in spreading the material when finally fouled for revivification.

It stands to reason that all processes for dealing with the sulphuretted hydrogen are much more easily carried out with the gases from continuous stills, like Grüneberg's, Feldmann's, etc., than with those from intermittent stills.

Very interesting are the statements on the results of dealing with the foul gases, sulphuretted hydrogen, etc., from ammonia-works, found in the *Reports of the Alkali Inspectors.* We here quote those found in the *Report*, No. 43, for 1906, pp. 67, 73, 79, 96, 103, 113, 125, 141, 153; I combine these into the following table:[1]—

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[1] The figures given in the last *Reports* were not yet in my hands when that table was drawn up, but they do not to any material extent differ from those here given.

Method of Destruction of the Foul Gases.	Percentage of Ammonia dealt with by the various Methods in District.								
	No. 1.	No. 2.	No. 3.	No. 4.	No. 4A.	No. 5.	No. 6.	No. 7.	Scotland.
By combustion	0·5	...	...	...	5·9	...	23·0	2·8	8·8
To vitriol chambers	...	11·8	...	27·1	20·0	...	6·7	67·9	...
By Claus process	...	16·4	2·0	13·4	26·5	15·2	5·3	12·0	13·0
In oxide-of-iron or lime-purifiers	89·1	32·9	39·8	36·4	47·6	30·5	64·6	8·9	70·0
To hydraulic main	...	...	...	...	..	..	...	0·6	...
By treatment with gas-liquor and subsequent combustion	...	36·9	...	...	...	3·7	...	...	...
By combustion of the H_2S and arrest of the SO_2 in limestone towers	...	...	...	...	...	1·5	0·4	7·8	...
By various processes	...	...	...	23·1	...	42·9	...	..	...
Retained by metallic salts	10·4	2·0	58·1	...	...	...	...	...	7·7
No H_2S generated, by the use of special processes	...	...	...	...	...	6·2	...	...	...

According to the *Reports* (*e.g.*, No. 28, pp. 57, 66, 87, etc.), the majority of works, in some districts two-thirds, burn the H_2S for the production of sulphuric acid, usually by introducing it into pyrites-burners; the others mostly use oxide-of-iron purifiers, a few the Claus process, and some burn the H_2S into SO_2, which escapes into the air. In one of the largest districts, producing 39,400 tons sulphate per annum, in 1893 (*Alkali Report*, No. 30, p. 100) 60·8 per cent. of the H_2S was converted into sulphuric acid, 11·6 into sulphur by the Claus process, 9·5 removed by oxide of iron, 18·9 burned and allowed to go into the air. In another district in 1894 (*Report* No. 31, p. 15), two works employed milk-of-lime and ferrous sulphate, two employed the H_2S for removing arsenic from sulphuric acid, 71 burned it and sent the SO_2 into the air, 23 made sulphuric acid from it, 24 employed the Claus process, 276 oxide-of-iron purifiers, 51 lime-purifiers.

According to *Report* No. 31, p. 98, the *cost* of removing the H_2S was as follows:—With oxide-of-iron purifiers in seven cases: 2s. 6d., 1s. 6d., 3s. 4d., 3s., 5s. 5d., 7s. 1d., and 3s. 6d., including interest and amortization; with the Claus process in five cases: 8d., 1s. 1d., 11½d., 1s. 1d., 1s. 1½d. In no case was a real profit made.

Stevenson (*Gas World*, 1895, p. 705) gives a calculation for the conversion of sulphuretted hydrogen from gas-liquor into sulphuric acid. In the course of a year 1977 tons of sulphuric acid (of what strength?) was made, and for this was used: 1023 tons pyrites 40 per cent., 99½ tons nitrate of soda, 342½ tons coke, £291 wages, £602 repairs, £300 5 per cent. interest on £5000; also the H_2S from 32,549 tons gas-liquor. Over and above the interest, a profit of £330 was made.

CONCENTRATION OF AMMONIUM SULPHATE SOLUTIONS.

We have spoken of this operation several times in the preceding description of various processes. Here we will only mention that it is generally carried out in leaden pans, heated by leaden steam-coils. Iron is not a suitable material in this case, as it is acted upon by ammonium salts, especially at higher temperatures, owing to the escape of a little free ammonia. Even if this action were so slight that it would do no serious injury to the apparatus (and this would most easily happen to wrought-iron steam-coils and the like), the iron would cause a discoloration of the ammonium salts, and reduce its commercial value. It is doubtful whether this could be entirely avoided by the proposal of P. S. Brown (B. P. 804, of 1878) to use boiling-pans made of iron, taking care to keep the liquid always slightly alkaline. Holmes (U.S. P. 1126471) for the same purpose (especially when evaporating solutions of ammonium nitrate) adds to the liquid about 0·5 per cent. of $Al(OH)_3$.

The smell arising from the evaporation of the sulphate liquors, where strong acid is not used, has been already mentioned. This smell has been likened to the odour from ill-kept pigsties, and sometimes this vapour may be a nuisance at a distance of 200 yards or more—nearly as much as the saturator-gases. To obviate it, steam should be driven through the saturator for twenty minutes or half an hour before running off the finished solution into the evaporating-pans; and this steam should be carried off and condensed in the usual way (*Dr Ballard's Report*, p. 135).

MANUFACTURING SULPHATE OF AMMONIA OTHERWISE THAN FROM AMMONIACAL LIQUOR.

A somewhat considerable quantity of sulphate of ammonia is recovered by washing spent oxide of iron from gas-purifiers and evaporating the washings. This salt is, however, very impure (*vide infra*).

Fogarty (B. P. 13747, of 1887) produces ammonium carbonate by burning "alkalized coal" in an atmosphere of air, steam, and nitrogen, and allows it to be absorbed by a mixture of calcium sulphate and sawdust, from which afterwards the ammonium sulphate is obtained by lixiviation.

Roustan (Ger. P. 46135) purifies coal-gas by a mixture of liquid calcium oxychloride, or calcium chloride and magnesia, with slaked lime and coke. The NH_3 condenses therein as carbonate, which is driven out by heating to a red-heat, and is absorbed in sulphuric acid, or condensed by cooling.

Eastman (B. P. 10192, of 1888) mixes coal-tar, heated to 37° C., with calcium sulphate and water; the aqueous liquid separating contains ammonium sulphate. F. H. Davis (B. P. 101976, of 1890) employs a similar process, but substitutes for the calcium sulphate a solution of copper or zinc sulphate. Both inventors evidently principally aim at the production of purified tar. The ammonia recovered will be hardly worth the expense.

Examination of Commercial Sulphate of Ammonia.

The properties of pure ammonium sulphate have been described *supra*, pp. 1319 *et seq.* Commercial sulphate is tested, first for its percentage of ammonia, secondly for impurities. The estimation of the *percentage of ammonia* is performed by one of the methods described in Chapter XIV., pp. 1270 *et seq.*

Ammonium sulphate is always sold according to its percentage of nitrogen or ammonia. Chemically pure salt would test 21·21 per cent. N, or 25·75 per cent. NH_3, and even commercial salt sometimes tests 24 or 25 per cent. NH_3.

In the English trade the strength usually stipulated for between buyer and seller is 23 per cent. NH_3. As the manufacturers found that they could get up to 25½ per cent., they brought this down to 23 per cent. by adding common salt or sulphate of soda; but some buyers object to this in the sale note (private communication from Mr Watson Smith).

Milburn (*Chem. Trade J.*, 1915, lvi., p. 285) states that, while the ammonia content of German sulphate is from 24¾ to 25 per cent., that from British manufacturers is usually only about 24 per cent.; and the latter often contains so much free acid that the cargoes despatched in bags not unusually arrive at their final destination practically in bulk, entailing heavy expenditure, and loss in weight and tests. He recommends to the British manufacturers improving their plant, and using more care in the work.

According to *Chem. Trade J.*, 1914, lv., p. 458, the Chairman of the British Sulphate of Ammonia Association has issued a circular to the members, urging them to improve the quality of the product, by making sulphate of ammonia testing from 24¾ to 25 per cent. ammonia, with not over 3 per cent. moisture, and not more than ½ per cent. free acid; if possible to adopt 25 per cent. NH_3 as a selling basis.

Sometimes the strength of commercial sulphate of ammonia is not quoted as percentage of ammonia, but (especially in Germany) as percentage of nitrogen.

The following table will help to quickly reduce either of these terms to the other:—

Table for comparing the Percentage of Nitrogen and that of Ammonia.

N.	NH_3.	N.	NH_3.	N.	NH_3.	N.	NH_3.
0·1	0·12	0·9	1·09	8	9·71	16	19·43
0·2	0·24	1	1·21	9	10·93	17	20·64
0·3	0·36	2	2·43	10	12·14	18	21·85
0·4	0·49	3	3·64	11	13·35	19	23·07
0·5	0·61	4	4·86	12	14·57	20	24·29
0·6	0·73	5	6·07	13	15·78	21	25·40
0·7	0·85	6	7·29	14	17·00		
0·8	0·97	7	8·50	15	18·21		

Moisture.—According to A. Schaefer (*Einrichtung und Betrieb eines Gaswerkes*, 3rd edition, p. 469) commercial sulphate of ammonia should not contain upwards of 2 per cent. moisture.

The *drying of the salt*, if necessary, can be effected in stoves, heated by the waste heat of some flue or by exhaust steam from an engine, or on open floors or plates heated from below.

Free Acid.—The ammonium sulphate, as it comes from the saturators, is often merely drained and sold in the moist state; in this case it will be very perceptibly acid. This can be avoided by carefully washing it, with very little water, on the drainer, but more easily by employing a centrifugal machine lined with lead, in which also the washing can be performed.

The sulphate intended for agricultural purposes should not contain any large proportion free acid, as any considerable quantity of this would damage the vegetation. The amount of free acid does not usually exceed 1·5 per cent. SO_3, and up to this percentage it seems to be harmless; on soil containing calcium carbonate even more than that, up to 3 per cent. SO_3, may be harmless.

Colour.—The commercial salt, when made with sulphuric acid free from arsenic and iron, should be white, or at least light grey. The salt made by direct saturation of gas-liquor with sulphuric acid is, of course, dark grey or brown; and even that made by distilling ammonia into sulphuric acid has a dark colour, unless precautions are taken against this by the mode of saturating the liquor (p. 1485). The German Coking-Committee (as mentioned by Leo in *Stahl u. Eisen*, 1914, p. 439), attributes the colour of ammonium sulphate to deficiencies in cooling the gases, or else to impurities of the sulphuric acid. It must also be noted that the sulphate made in the more perfect apparatus, as those of Grüneberg, Feldmann, and others, is much less liable to be coloured, because the tarry impurities are mostly condensed in the dephlegmating-columns. But even then the sulphate may, after some time, assume a yellow colour from iron salts gradually accumulating in the saturator; this is avoided by cleaning the latter out from time to time. Sulphide of arsenic also causes a yellow colour, and for this reason many English manufacturers employ brimstone-acid (p. 1465); but even in Germany, where pyrites-acid is exclusively used, the sulphate is usually not yellow, partly because sulphuric acid made from purer pyrites is generally employed, partly because the arsenious sulphide can be skimmed off during saturation, sometimes with special additions (p. 1466).

Sometimes the sulphate shows a more or less pronounced *blue* colour, which gives trouble in disposing of it. The first mention of this is found in *Chem. Zeit. Rep.*, 1866, p. 282, but this subject has only quite recently evoked much attention, and has been treated at length by the Inspectors of Alkali Works in their annual reports for the years 1905 and 1906, especially by Mr Linder (*Rep.*, No. 42, pp. 51-62). Mr Carpenter, in No. 43, p. 30, sums up the results arrived at. The blue colour is caused by an insoluble *ammonium ferrous ferrocyanide*, precipitated together with the crystals of ammonium sulphate, and this will take place, if *local alkalinity* occurs at some part of the separator, especially in the neighbourhood of the pipe distributing the vapours containing volatile ammonium salts, ammonium cyanide being one of these. The first stage consists in the formation of ammonium ferrocyanide, which occurs by the separation of hydrated iron sulphide or oxide in suspension from the mixture in the separator, owing to that mixture becoming neutral or alkaline. This formation is favoured by low temperature, as the solubility of hydrocyanic acid is thereby increased; once this is fixed as ferrocyanide, no amount of subsequent boiling under ordinary pressure will remove it. In the second stage, with access of ferrous salts in acid solution, a *white* precipitate of ammonium ferrous ferrocyanide, insoluble in acid, is produced. This is not noticed on fishing out the crystals of ammonium sulphate, but on continuous exposure to the air the ferrous salt, a third reaction takes place, viz., oxidation to ferrocyanide, *i.e.*, Prussian blue. It is easy to examine the sulphate for the chance of turning blue on keeping by testing a sample of the fresh salt with hydrogen peroxide or another oxidizing agent.

Hence we may take it for certain that local alkalinity, coupled with low saturator temperature, are the conditions favouring the formation of blue sulphate. Priming over of ammoniacal liquor from the stills would produce both these conditions, but they can exist without priming having occurred. We may take the following equations as representing the three stages:—

(*a*) $6NH_4Cy + FeS = (NH_4)_4Fe(Cy)_6 + (NH_4)_2S.$

(*b*) $(NH_4)_4Fe(Cy)_6 + 2FeSO_4 = Fe_2Fe(Cy)_6 + 2(NH_4)_2SO_4.$

(*c*) $Fe_2Fe(Cy)_6 \rightarrow Fe_3(Fe(Cy_6)_2 \rightarrow Fe_4(Fe(Cy_6)_3.$

Cf. also Bailey, *J. Gas Lighting*, 1907, p. 522, who agrees with the above.

Impurities.—A most objectionable impurity in ammonium sulphate is *ammonium sulphocyanide* (thiocyanate). This is scarcely found in such salt as is obtained by distilling gas-liquor with lime and absorbing the gas in sulphuric acid; but it may occur in the salt obtained by direct saturation of gas-liquor with acid (p. 1329), and it is regularly found in the salt which is made by washing spent oxide of iron from purifiers and simply evaporating the washings (p. 1206). The latter product contains frequently 25, sometimes even up to 91 per cent. of sulphocyanide.[1] Since this salt is very injurious to vegetation,[2] and lessens the value of ammonium sulphate, or even makes it quite unsuitable for manuring-purposes, such solutions from spent oxide ought never to be utilized by direct evaporation, but should be distilled with lime; from the residue calcium sulphocyanide may be extracted, and may be worked up into sulphocyanides, which have now become articles of commerce.—The detection of sulphocyanide in commercial sulphate is easily made by the well-known red colour which it gives with ferric chloride.

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[1] Esilman & Bell, *Chem. News*, xxxii., pp. 124, 197.

[2] The damage done to plant-growth by ammonium sulphocyanide (thiocyanate), which was considered a matter of notoriety, has been represented as slight by Mr Maerker (Biedermann's *Centralblatt für Agrikulturchemie*,

P. G. Lloyd (*Chem. News*, 1908, xcviii., p. 172) points out that for some years past commercial sulphate of ammonia has rarely contained any appreciable quantity of sulphocyanides, but sometimes it contains *organic compounds injurious to plant life*, probably owing to their influence on the nitrifying organisms. Gas sulphate sometimes shows this action in special cases, but bone sulphate does not, although very strongly coloured. His assistant, Dr Bonelli, found the following test for this. If 1 g. of the sulphate is dissolved in 5 c.c. water and strong ammonia added, an intense violet coloration is produced where the undesirable organic compounds are present, while no change occurs either with pure gas sulphate or bone sulphate. To detect sulphocyanides in the presence of those organic compounds, moisten 5 g. of the sulphate of ammonia with strong ammonia, dry in a water-oven, grind with 5 c.c. alcohol, filter, dilute the alcoholic filtrate with water, and test with ferric chloride, which gives the usual bright red coloration if sulphocyanides are present.

Prescriptions laid down in Sale-notes for Sulphate of Ammonia.

The following prescriptions have been issued by the German Union for the sale of ammonia:—

1. *Sampling on loading the Salt.*—From each transportation vessel or bag a sample of the same volume is taken by means of a ladle or auger; these samples are collected in a vessel

1883, p. 494). But the researches of P. Wagner (*ibid.*, 1873, p. 336), of C. Schumann (*ibid.*, 1882, p. 332), and of C. Böhmer (*Wagner-Fischer's Jahresber.*, 1884, p. 324), on the contrary, fully prove the injurious action of the sulphocyanides on plants.

provided with a tightly closing lid, the contents of which are as soon and as quickly as possible ground up and well mixed. From this the samples are taken for buyer and seller, into glass bottles sealed by the seller.

2. *Analysis.*—Twenty-five g. of the sample are quickly weighed out on a sufficiently accurate balance, and washed by distilled water into a half-litre flask, which is then filled up to the mark. From this the samples are taken for the following tests:—

(*a*) *Ammonia* is estimated by distilling 50 c.c., after adding 20 c.c. cold, boiled-out caustic-soda solution (120 g. NaOH per litre), in the usual way (*supra*, p. 1270). The distillate is caught in 40 to 43 c.c. normal sulphuric acid, and the non-saturated acid retitrated in the cold with normal caustic-soda solution, using as indicator 2 drops of a solution of 1 methyl-orange in 1000 water (which may be added already to the normal acid).

(*b*) *Free acid* is found by titrating 100 c.c. with decinormal caustic-soda solution, in the cold, with methyl-orange as indicator.

(*c*) *Moisture.*—Fifty g. of the salt are weighed on a good balance and dried at about 100° in a stove up to constancy of weight.

(*d*) The *deciding tests* are made upon the samples, taken at the ammonia works by persons of confidence, and at the public laboratory agreed upon between buyer and seller.

According to the *Chem. Trade J.* of 31st July 1915, lvii., p. 100, the British Sulphate of Ammonia Association are urging the British manufacturers of that article to turn it out testing 25 per cent. ammonia, which at present is the case only with about 10 per cent. of the British sulphate of ammonia, whilst it is the regular strength in Germany, and about half the world's production is now sold on a 25 per cent. basis (*vide supra*, p. 1513).

Applications of Sulphate of Ammonia.

1. Most of the ammonium sulphate is employed as a fertilizer; for the cultivation of beetroot especially it cannot be replaced by

the cheaper nitrogen of nitrate of soda; hence the very large importation of this salt into Germany (*cf.* p. 1524). The action of ammonia as fertilizer is slower than that of nitrate of soda, but all the more lasting. It is absorbed by the soil and retained even after large quantities of rain have come down, whereas nitrate of soda is washed out in this case, and its soda also renders the soil in the end too hard for tilling. According to the kind of crop and the conditions of clime and soil, either ammonium sulphate or sodium nitrate will be best to apply. On the whole, ammonia is preferable for potatoes; for wheat, rye, and oats, they are of equal value.

The sulphate also serves for preparing the other ammonium salts, and sometimes for liquor ammoniæ, and for making ammonia-alum. In the manufacture of ammonia-soda, the sulphate is now mostly replaced by the cheaper concentrated gas-liquor (pp. 1344 *et seq.*).

A 10 per cent. solution of ammonium sulphate is employed to render tissues, papers, etc., non-inflammable. Beaulieu-Marconnay (Ger. P. 152006) applies the sulphate for this purpose, mixed with borate and free ammonia, which at the same time renders the timber less hygroscopic, and allows of carrying on the process below 50°. The best mixture is: 1 part ammonium sulphate and 3 parts boric acid, both in the solid form, dissolved in an excess of liquor ammoniæ.

Steinherz (Ger. P. 287744) employs for this purpose a solution of 5 per cent. ammonium sulphate and 20 per cent. magnesium sulphate.

Synthetical urea is made from a solution of crude potassium cyanate (prepared by fusing 8 parts dehydrated prussiate of potash with 3 parts carbonate of potash and 15 red lead), adding to it a quantity of ammonium sulphate equal to that of the prussiate of potash used, concentrating the solution by evaporation, separating the liquid portion from the potassium sulphate crystallizing out, boiling down to dryness, and extracting the urea from the dry residue by means of alcohol.

A very important application for ammoniacal nitrogen seems to be in store for the manufacture of nitric acid from ammonia, as described in *Lunge's Sulphuric Acid and Alkali*, 4th edition, i., pp. 253 *et seq.* (1913).

Statistics on the Manufacture of Sulphate of Ammonia.

Great Britain.—The following table is compiled from the *Alkali Inspectors' Reports*, and the reports of Bradbury & Hirsch, Liverpool. The figures mean long tons, and comprise all ammonia, calculated as sulphate:—

From	1893.	1894.	1895.	1896.	1897.	1898.	1899.
Gas-works . .	87,000	113,634	119,645	127,498	132,724	129,590	136,529
Blast-furnaces . .	5,500	10,075	14,588	16,511	17,772	17,935	17,963
Shale-distilleries .	22,000	32,298	38,325	37,822	37,153	37,264	38,780
Gas-producers, coke-ovens, etc. . .	3,000	3,448	7,083	9,078	10,624	11,568	15,209
Total . .	117,500	159,455	179,641	190,909	198,273	196,357	208,481

From	1900.	1901.	1902.	1903.	1904.	1905.	1906.	1907.
Gas-works . .	142,419	142,703	150,055	149,489	150,208	155,957	157,160	165,474
Iron-works . .	16,950	16,353	18,801	19,119	19,568	20,376	21,284	21,024
Shale-works .	37,267	40,011	36,931	37,353	42,486	46,544	48,534	51,338
Coke-oven works .	10,393	12,255	15,352	17,438	20,848	30,732	43,677	53,572
Producer-gas and carbonizing works (bone and coal) . .	6,688	5,891	8,177	10,265	12,880	15,703	18,736	21,873
Total . .	213,717	217,213	229,316	233,664	245,990	269,112	289,391	313,281

From	1908.	1909.	1910.	1911.	1912.	1913.	1914.
Gas-works . .	165,218	164,000	168,000	169,500	172,094	182,180	175,939
Iron-works . .	18,131	20,000	21,000	20,000	17,026	19,956	16,088
Shale-works .	53,628	57,000	60,000	60,000	62,749	63,061	62,207
Coke-oven works .	64,227	107,500	120,000	129,000	104,932	133,816	137,430
Producer-gas and carbonizing works (bone and coal) . .	24,024				32,049	33,605	32,049
Total . .	325,228	348,500	369,600	378,500	388,850	432,618	423,704

Of the quantity made in 1914, England contributed 295,000 tons, Scotland 123,000 tons, and Ireland 3000 tons.

The following table shows the amount of ammonium sulphate *exported* from Great Britain to other countries, expressed in units of 1000 tons:—

Year.	Germany and Belgium.	Spain and Portugal.	France.	Java.	Holland.	United States.	British Guiana.	West Indies.	Other Countries.	Total.	Home Consumption.	Percentage of Exportation.	Percentage of Home Consumption.
1894	41·5	17·4	8·8	6·2	11·9	4·3	5·3	3·7	4·2	103·3	56	64·85	35·15
1895	40·3	22·2	7·3	5·9	7·1	11·6	6·2	2·4	8·7	111·7	67·8	62·23	37·77
1896	43·4	21	12·8	8·3	7	9·8	6·8	4·3	12·6	126	64·5	66·14	33·86
1897	55·2	27·2	23·1	6·8	9·8	8·9	4·9	4	13·1	153	45	77·27	22·73
1898	42·2	31·5	16	18·3	10·2	4·7	6·3	4·9	12·8	136·9	59·6	69·67	30·33
1899	33·6	38·3	10	13·6	8·4	8·2	5·2	4·8	18·13	140·2	65·3	68·22	31·78
1900	32·6	37·5	11·7	11·5	10·3	9·5	7·6	5·5	19·1	145·3	67·7	68·22	31·78
1901	41·6	36·9	6·7	14·2	(?)	10·6	(?)	(?)	(?)	150·2	63·5	70·29	29·71
1902	44·1	40·3	12·6	15·5	7·2	10·1	7·1	4·5	21·4	162·8	68·7	73·5	26·5
1903	35	43·6	9·6	19·3	7·9	8·4	7·8	3·6	27	162·2	61·8	73·6	26·4
1904	31	48	10·5	21·5	11·6	9·4	...	...	...	177·3	...	...	...
1905	...	...	...	...	...	...	...	...	...	...	...	...	...
1906	...	...	...	...	...	...	...	...	...	201·5	...	...	...
1907	...	...	...	...	...	...	...	...	...	230	...	...	...
1908	33·5	51·7	23·6	13·4	3·3	28·9	8·1	4·0	8·0	234·9	...	...	...
1909	37	66·1	12	23·0	7·1	35·1	8·1	5·1	8·9	264	...	...	...
1910	7·5	50·2	8·4	32·4	3·4	76·1	7·5	5·3	12·6	283·8	...	...	...
1911	2·7	...	...	...	...	...	...	...	...	291·9	...	...	...
1912	2·1	64·3	7·7	33·5	...	39·3	...	...	40·6	289·5	...	...	...
1913	14·5	55·9	8·9	38·0	2·2	37·0	...	...	...	328·2	...	...	...
1914	...	...	...	...	...	...	...	...	...	314	...	...	...

Iron-works recovering ammonia from blast-furnaces in the United Kingdom are almost exclusively confined to Scotland, as only in special districts coal is hard enough to stand in the blast-furnace without crushing. The English works are confined to Staffordshire. The production from shale distillation is entirely confined to Scotland. The most remarkable development concerns the coke-oven works, as is apparent from the above given table.'

In District No. 2 (North of England), where liquor corresponding to 29,666 tons of sulphate of ammonia was distilled in 1906, only 0·17 per cent. of this was made into liquor ammoniæ. Fifty-seven works used continuous distillation, representing 99·7 per cent. of the liquor distilled; eight small works used discontinuous distillation. This proportion was almost the same in the other districts, the proportion of liquor distilled by continuous processes being from 99·1 to 99·5 per cent. of the total.

The number of ammonia-works (sulphate, muriate, and gas-liquor) in the United Kingdom in 1906 was 536, in 1907, 554; in 1909, 536 works produced ammonium sulphate and chloride, and 57 works only concentrated liquor ammoniæ; in 1910 the former had increased to 543, the latter had decreased to 55.

From the report of the Chief Inspector of Alkali Works, W. S. Curphey, *J. Gas Lighting*, 1911, cxv., p. 13, we take the following statements upon the sources from which the ammoniacal liquor produced in the United Kingdom was obtained:—

	1909. Per cent.	1910. Per cent.
Gas-works	54·9	51·2
Coke-works	34·0	35·2
Power gas-works	6·9	9·9
Iron-works	2·8	2·3
Carbonizing-works for bones and coal .	1·4	1·4

United States.—The production of ammonia in the United States, expressed in its equivalent of sulphate, according to *The Mineral Industry*, xv., p. 28, has been:

	1898	1899	1900	1901	1902	1903	1904
Short tons . .	17,000	19,500	27,600	29,279	36,124	41,873	54,664

	1905	1906	1907	1908	1909	1910
Short tons .	65,296	75,090	89,000	83,100	106,500	116,000

At the present time about three-fourths of the ammonia comes from by-product coke-ovens.

The following table shows the imports, the total consumption, and the average market price per short ton of 2000 lb. in the United States:—

	1899.	1900.	1901.	1902.	1903.	1904.	1905.	1906.	1907.
Imports (short tons) . .	6,976	8,411	14,486	18,146	16,777	16,667	15,288	9,182	30,114
Total consumption (short tons) . ..	26,476	36,011	43,765	54,290	58,650	71,331	80,584	84,182	119,814
Market price .	$50·29	$57·40	$55·16	$59·90	$62·10	$61·71	$62·92	$62·33	$64·93

In 1912, the United States imported 54,015 tons; in 1913, 62,190 tons; in 1914, 78,042 short tons of ammonium salts, calculated as sulphate.

Germany.—N. Caro (*Die Stickstofffrage in Deutschland*, 1908, p. 18) gives the following table for the production of ammonium sulphate in Germany:—

Year.	At Gas-works.	At Coke-works.	Total sulphate.	Liquor ammoniæ.	Excess of importations of sulphate from abroad over exportations.
	Tons.	Tons.	Tons.	Tons.	Tons.
1897	14,000	70,000	84,000	...	30,492
1898	14,000	84,000	98,000	...	26,172
1899	15,500	84,500	100,000	...	27,315
1900	18,000	88,500	106,500	580	20,674
1901	20,000	113,000	133,000	720	34,866
1902	23,000	117,000	140,000	1180	36,509
1903	26,000	120,000	146,000	1630	29,576
1904	30,000	152,000	182,000	1680	24,468
1905	35,000	168,000	203,000	2425	27,416
1906	38,000	197,000	235,000	2500	...

The following statements are from other sources (the figures mean thousands of tons):—

Year.	Production at gas-works.	At coke-works.	From Vinasse.	Total production.	Home-consumption.
		Per cent.	Per cent.		
1906	30	200	5	235	...
1907	30	257	...	287	...
1908	...	...	...	313	287
1909	40	278	5	322	322
1910	40	...	...	373	...
1911	40	...	...	408	...
1912	...	...	...	492	...
1913	...	...	...	549	...
1914	...	...	...	414	...

It is expected that in Germany shortly, 300,000 tons per annum of ammonia in various forms will be produced, so that its total annual production will be equal to about 800,000 tons of sulphate.

The following figures show the importations and exportations of sulphate of ammonia for Germany for some years:—

	1904.	1905.	1906.	1907.	1912.	1918.
	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.
Importation . .	35,166	48,005	35,366	33,522	23,098	34,627
Of this from Great Britain . .	17,678	26,813	16,283	13,500	...	...
Of this from Austria	12,293	14,519	15,686	16,524	...	...
Exportation . .	10,696	27,589	37,288	57,493	57,267	75,868
Of this to Belgium .	5,219	18,078	23,692	30,940	19,723	15,774
" " France .	371	1,027	2,629	7,242	4,213	7,428
" " Italy .	6	279	3,601	6.507	3 016	3,550
" " Netherlands . . .	1,345	1.167	4 691	11,756	19,121	18,195

Consumption of ammonium sulphate in Germany:—

Year.		Year.	
1908 . . .	275,000 tons	1910 . . .	370,000 tons
1909 . . .	350,000 "	1911 . .	415,000 "

Italy (*Chem. Ind.*, 1908, p. 523) produces about 5000 tons, and imports another 4000 tons, nearly all from England.

In *Chem. Trade J.*, xliii., p. 150, we find the following official statements for the production and importation of sulphate of ammonia in Italy:—

Year.	Productions.	Imports.	Total.	Year.	Productions.	Imports.	Total.
	Tons.	Tons.	Tons.		Tons.	Tons.	Tons.
1896	1,523	...	...	1902	3,449	5,501	8,941
1897	1,606	...	...	1903	3,686	5,367	9.053
1898	1,350	3.858	5,208	1904	3,837	6,975	10,812
1899	1,436	4,504	5,940	1905	4.124	5,201	9,325
1900	2,147	5,362	7,509	1906	4,820	9,738	17,558
1901	2,967	4,297	7,264	1907	...	14,942	...

In 1912 Italy imported 21,190 tons, and exported 21,669 tons sulphate of ammonia.

Austria-Hungary produced sulphate of ammonia:—

Year.	Tons.	Year.	Tons.	Year.	Tons.
1898 . . .	30,000	1901 . .	40,000	1906 . .	45,000
1899 . .	30,000	1902 . .	45,000	1907 . .	55,000
1900 . .	35,000	1903 . .	44,000	1908 . .	80,000
				1909 . .	97,000

France :—

Year.	Tons.	Year.	Tons.	Year.	Tons.
1898	35,000	1902	40,000	1906	49,000
1899	36,000	1903	42,000	1907	52,700
1900	37,000	1904	43,000	1908	52,000
1901	38,000	1905	47,300	1909	53,000
				1910	56,000

Belgium and Holland :—

Year.	Tons.	Year.	Tons.	Year.	Tons.
1898	30,000	1902	38,000	1906	30,000
1899	32,000	1903	35,000	1907	55,000
1900	33,000	1904	39,000	1908	35,000
1901	35,000	1905	24,000	1909	40,000

World's Production.—The following estimate of the world's production of ammonium sulphate is taken from various sources. The figures up to 1911 mean long tons, those for 1912 and 1913 metric tons (=2204·6 lb.).

Country.	1902.	1903.	1904.	1905.	1906.	1907.
Great Britain	225,300	230,200	241,500	264,400	279,000	331,220
Germany	135,000	140,000	173,000	190,000	235,000	287,000
United States	33,000	38,000	50,000	60,000	68,000	81,400
France	40,000	52,000	43,000	47,300	49,100	52,700
Belgium and Holland	38,000	35,000	39,000	24,200	30,000	55,000
Other countries	45,000	45,000	48,000	55,000	55,000	88,000
Total	516,300	540,200	594,500	640,900	716,100	895,320

Country.	1908.	1909.	1910.	1911.	1912.	1913.
Great Britain	321,000	348,000	369,000	378,500	394,226	438,932
Germany	313,000	340,000	383,000	418,000	492,000	549,000
United States	40,000	90,000	116,000	115,000	149,700	176,900
France	52,000	53,000	57,000	60,000	69,100	75,400
Belgium and Holland	35,000	40,000	41,000	40,000	43,700	48,600
Other countries	97,000	107,000	145,800	169,500	100,700	123,200
Total	858,000	978,000	1,111,800	1,181,000	1,249,426	1,412,032

CHAPTER XV

THE WORKING-UP OF AMMONIACAL LIQUOR INTO CONCENTRATED LIQUOR AND LIQUID AMMONIA

Storing and Separating from the Tar.

According to the nature of things, ammoniacal liquor, such as results from mixing up the aqueous liquids from the hydraulic main, condensers, and scrubbers, is always more or less contaminated by tarry substances. Some of these are actually dissolved in the water; but others are only present in the state of suspension, and can be separated by proper settling. It is very important that this should be done, as the nuisance caused by working ammoniacal liquor is very much lessened by the removal of these tarry substances.

The separation of tar and ammoniacal liquor is principally effected in the collecting-basins of gas-works and coke-works, as described in Vol. I., pp. 378 and 384, sometimes aided by special contrivances (Vol. I., pp. 385 *et seq.*). But there always remain small quantities of tarry substances suspended in the aqueous liquor, which in its working up for ammonia may cause great trouble by forming with part of the lime, introduced into the stills, greasy masses, sticking fast in the various parts of the apparatus, and causing frequent interruptions of work by the necessity of removing them.

Of course it is very important to completely remove these tarry substances before working up the ammoniacal liquor, either by prolonged sedimentation or by special contrivances.

An excellent arrangement for this purpose is in operation at the Vaugirard gas-works at Paris, where formerly strong complaints were made by the neighbours. It is shown in Figs. 254 and 255, p. 1328, in vertical section and ground-plan. The gas-liquor is stored in large underground brickwork cisterns, GG, and is from these pumped by pumps TT (driven by the steam-engine M) into the four iron tanks B, C, D, E, mounted at a height. These tanks communicate by overflows; the liquor is first pumped into B, and from there gradually runs into C, D, and E. During this passage the settling down of the tar takes place. Most of it is found in B and C, very little in the others. The liquor, now practically free from tar, runs from the surface of the last settler, E, through the pipe S, into the gauging-tank from which the stills are charged. The tar collecting at the bottom of the first two settlers, B, C, is drawn off by the tap F, and run into iron tank-wagons, to be transported to the tar-works. The small quantity of tar collecting in D and E is run back into the cisterns GG by means of the pipes I, I′, and K.

At large gas-works sometimes the tar and ammoniacal liquor, which are produced in about the proportion 1 : 2, are first stored in smaller pits, sufficing for about a week, and then pumped up into high-level tanks, as just described.

The brickwork of the tanks for ammoniacal liquor should be made with asphalte mortar, or there should be at least an outward isolating space of an inch, filled up with asphalte. The tank bottoms are inclined to one side; at the lowest point there is a small collecting-tank for the tar separating here. The liquor goes through a coke filter, for retaining any coarser impurities, through a pipe to the bottom of the first tank, from this in the same way into the second tank, and so forth; from the last tank, which contains perfectly clear liquor, it is pumped into the stills.

The Deutsche Continental Gas-Gesellschaft in Dessau (Ger. P. 191342) separates the ammoniacal liquor from the tar by allowing this to flow downwards in an open, inclined spout which passes through the liquor and the tar, contained in a tank, part of the spout being free on the top. Here the ammoniacal liquor, being of smaller specific gravity, separates from the tar and is at once taken up by the liquor in the tank, when touching it. The tar continues its course downwards in a quiet stream, until it unites with the tar below. For each of these liquids overflows are arranged.

Brunck (B. Ps. 8287, 1903; 15646, 1905; Fr. Ps. 331077

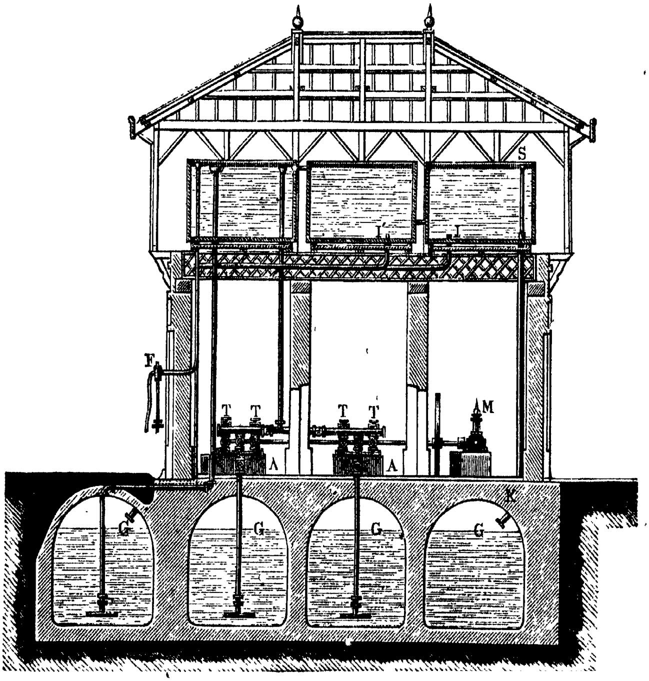

FIG. 254.

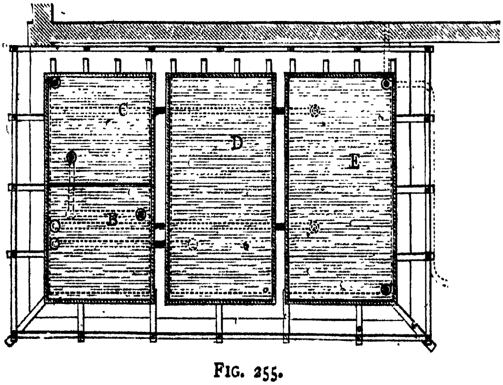

FIG. 255.

and 356589; U.S. Ps. 824902 and 825297) subjects the gases to centrifugal action, in order to free them from tarry matters, before they enter the absorption apparatus for ammonia.

Storage.—On a soil liable to changes of level, as is frequently the case near coal-pits, the ammoniacal liquor is preferably stored, not in brickwork tanks, but in iron tanks, set in such manner that they can be inspected and caulked in case of need.

If gas-liquor has to be kept in stock for any length of time, it must not be forgotten that it loses a great deal of its ammonia by evaporation. This loss may to a great extent be avoided by running in the fresh liquor near to the bottom of the tank, and pumping it away from the same place. Thus the upper portion of the contents of the tanks remains very nearly unchanged for a long time, and protects the lower portion from a loss of ammonia by evaporation.

A process for storing ammoniacal liquor (as well as tar, etc.), in a proper manner is the subject of the Ger. P. 204888, of 1906, by Ernst Körting. He forces the liquid with exclusion of air into a tightly closed store-tank, the gas space of which is connected with a coal-gas pipe, in order to prevent rusting of the inside metal, as well as losses by evaporation and nuisance by escaping gases.

Working-up Ammoniacal Liquor without Distillation.

Sometimes crude gas-liquor is *directly used as manure;* but its carriage would form an obstacle to a more extended employment of this kind, and the inevitable loss of ammonia by evaporation is also a disadvantage.

Formerly, the most usual method of treating so much of the gas-liquor as was not run to waste was to *saturate it directly with sulphuric or hydrochloric acid,* and to evaporate the solution till the ammonium salt crystallized out. The gases escaping at the saturation, carbon dioxide and hydrogen sulphide, were sometimes passed through a fire to burn the hydrogen sulphide, which was done very imperfectly, owing to the admixed moisture and carbon dioxide. The resulting sulphate or chloride of ammonia was very much discoloured by tarry substances, and at the present day would hardly be saleable. Apart from this, direct saturation must be declared irrational, because the evaporation of such dilute solutions takes more fuel than the driving-off of ammonia in properly constructed apparatus; and there is, moreover, a smell of H_2S during the concentration of the liquors. Direct saturation seems to be rarely, if at all, practised now for sulphate, but it is still done for ammonium chloride.

A certain modification of the direct saturation process is practised by Hepworth (*Twenty-third Report on the Alkali Acts*, p. 38). The scrubbers are fed with a neutral solution of sulphate of ammonia, which, after having taken up the ammoniacal compounds, is neutralized in leaden vessels with sulphuric acid of sp. gr. 1·7, the escaping gases being passed through an oxide-of-iron purifier. The neutral solution is again pumped up, and this is continued until the strength has risen to 1·20, whereupon the liquor is put into the evaporating-pans. The liquor should never be pumped upon the scrubbers in an acid state, which would cause a loss of illuminating-power to the gas.

This process in 1886 yielded 170 tons sulphate from 18,500 tons coal distilled; the gas daily passing through the scrubbers amounted to 800,000 or 900,000 cubic feet.

Treatment with Calcium or Magnesium Sulphate, etc.—The conversion of raw gas-liquor into sulphate is sometimes performed by bringing it in contact with calcium sulphate (plaster of Paris, gypsum); but this yields only a very impure article, and, cheap as this plan seems to be, is not carried out by any large number of works.

Al. MacDougall (B. P. 202, 1882) mixes calcium or magnesium sulphate or chloride with sawdust, bark, peat, or the like, and sprinkles the gas-liquor over it, after having added a little sulphuric or hydrochloric acid. Thus ammonium sulphate or chloride is produced.

De la Martellière (B. P. 2963, 1880) adds to gas-liquor aluminium sulphate, and draws off the resulting solution of ammonium sulphate from the precipitated silica and alumina, which carry down the tarry matters. The purport of this invention is not very clear, since this mode of purification from tarry matters would be rather expensive.

Dubosc and Henzey (*Bull. Soc. Ind. Rouen*, xvii., p. 439) treat gas-liquor with calcium chloride and ferric chloride, whereby the sulphide is removed, and evaporate the solution of ammonium chloride.

Pfannenschmidt (*J. Gasbeleucht.*, 1884, p. 205) recommends the following process for dealing with gas-liquor at small gas-works, where it does not pay to employ costly apparatus:—The spent oxide of iron is spread out in an open shed in a layer of 6 or 8 in., and soaked with as much gas-liquor as it will take up. Upon this another such layer is spread, equally soaked with this liquor, and this is several times repeated, the top layer remaining dry. After a few days the heap is turned over till dry, whereupon it will take up more liquor. This must be done in dry, warm weather. The ammonium sulphide first forms iron sulphide, and this is oxidized into ferrous sulphate. This again acts on ammonium carbonate and sulphide, with formation of ammonium sulphate and ferric hydrate, together with iron sulphate, which continues the process. Thus up to 32 per cent. ammonium sulphate can be accumulated in the mass. (No doubt much ammonia will be lost, and a very perceptible smell caused by this process.)

Grahn (*Chem. Zeit. Rep.*, 1888, p. 169) avoids distilling the gas-liquor by driving out the ammonia by a current of air, and applies heat in case of need. (This process must at all events leave all fixed ammonia behind, and the condensation of the volatile ammonium salts is thus rendered much more difficult.)

Warth (*Chem. News*, 1906, p. 259) proposes to use plaster of Paris for extracting the ammonia from gas-liquor in places where sulphuric acid is not available in large quantities. By shaking up liquor with plaster of Paris, he recovered 97 per cent. of the ammonia present, viz., 17 per cent. by boiling the solution and absorbing the evolved ammonia in sulphuric acid, and 80 per cent. by concentrating the residual solution to obtain crystallized ammonium sulphate. If it were desirable to dispense altogether with the use of sulphuric acid, the gas-liquor might be first treated with gypsum and the solution drawn off treated with ferrous sulphate, filtering off the FeS produced.

The Société Industrielle des Produits Chimiques Cuise-Lamotte (Ger. Ps. 253553 and 270532) passes into a saturated solution of ammonium sulphate NH_3 and CO_2 in equal molecular proportions and transforms the ammonium carbonate formed into sulphate by means of calcium sulphate. The liquid is heated, whereby the ammonium sulphate goes into solution, and can be separated from the calcium carbonate by filtration.

Kieserite (*native magnesium sulphate*), from Stassfurt, is employed by Kelly and Weigel (B. P. 8680, 1884) in this way:—A mixed solution of kieserite and common salt is cooled down, whereupon sodium sulphate crystallizes out. This is treated by ammonia and carbonic acid; the resulting sodium bicarbonate is separated by filtration, and from the mother-liquor ammonium sulphate is recovered. This is evidently more a process belonging to the domain of alkali-making. This is also the case with Gerlach's process (*Dingl. polyt. J.*, ccxxiii., p. 82), which is founded upon decomposing concentrated gas-liquor by sodium chloride, sulphate, or nitrate, and passing a stream of carbon dioxide into the liquor, whereupon sodium bicarbonate is precipitated, and ammonium chloride, sulphate, or nitrate remains in solution. This process has never been practically carried out.

N. Schuster and British Coke Ovens, Limited (B. P. 6061, 1914), extract ammonia from ammoniacal liquor by means of coal-gas from which the heavy hydrocarbons have been removed. For this purpose the necessary volume of gas is withdrawn from the main, is then reheated, and, after having been passed through an ammonia still in which it becomes heavily laden with ammonia, is returned to the main, and together with the gas flowing through the main is caused to enter a saturator. The returning gas laden with ammonia is caused to re-enter the main at a pressure greater than that of the gas at the part of the main where the returning gas so enters. As compared with the employment of steam for the extraction of ammonia from ammoniacal liquor, it is claimed that this process effects an enormous saving of heat.

A great deal of attention has been recently given to working up ammoniacal liquor without distillation by *oxidizing the ammonia into nitric acid.* Many years ago Kuhlmann showed that ammonia, under the influence of platinum sponge, is burned by atmospheric oxygen into nitric acid; but the technical utilization of this reaction dates only from the last ten or twelve years. The following processes are founded upon it.

Ostwald (B. Ps. 698 and 8300, of 1902; 7909, of 1908; U.S. P. 858904) with the co-operation of Brauer, found as best atalyser for this reaction platinum foil, covered with platinum black, which allows of utilizing gaseous mixtures containing but a small percentage of ammonia. Gas-liquor, putrefied sewage, etc., are mixed with a sufficient quantity of caustic lime or soda, and treated with air on the counter-current principle. There must be at least 7O for $2NH_3$, to produce $2NO_2+3H_2O$. The gaseous current must have a certain rate of speed, and the contact mass a temperature over 300°. The nitric acid formed s obtained in the shape of ammonium nitrate. Ostwald's process has been carried out on a large scale by the Gewerkschaft Lothringen at the Mont Cenis coal-pit.

A similar process is that of Schmidt and Böcker (*Berl. Ber.*, 1906, p. 1366).

K. Kaiser (B. P. 20305, of 1910) preheats the air before mixing it with the ammonia gas, and passes it over finely meshed platinum tissue, either left smooth or platinized.

Frank and Caro (Ger. P. 224329) employ as contact substance for the oxidation of ammonia thorium oxide by itself, or mixed with other oxides of the rare earths; this has the advantage against other catalysers of swelling up by the formation of thorium nitrate, and therefore always remaining n an active form.

Wendriner (*Chem. Ind.*, 1911, p. 456) employs as contact substance uranium, or compounds of it, by themselves or mixed with other catalysers; the reaction in this case goes on at 400° to 500°, with nearly theoretical yield.

Removal of the Cyanides from Gas-liquor before Distillation.

Bower (B. P. 2918, of 1882) converts the cyanide in raw gas-liquor into ferrocyanide before distilling it with lime.

Gutknecht (B. P. 9396, of 1903) also purifies the crude gas-liquor from cyanides and H_2S by addition of ferrous sulphate, so as to make it fit for fresh use. When thus enriched, he treats it with calcium sulphate and recovers the ammonium sulphate thus formed by evaporation. From the iron precipitate he recovers sulphate, ferric oxide, and Prussian blue.

Herry (Fr. P. 403056) treats the gas-liquor with carbon dioxide, in order to convert the ammonium sulphide into carbonate, adds sodium carbonate in order to decompose the cyanides, thiocyanates, etc., and obtains crystallized ammonium carbonate by concentrating the solution.

J. Grossmann has worked out a very interesting process for removing the cyanides, for which he has taken out the B. P. 19988, 1907, and upon which he has published a paper in the *J. Soc. Chem. Ind.*, 1908, pp. 393 *et seq.* The claims of the patent are: (1) The conversion of the cyanide compounds in crude ammonia liquors into ferrocyanide by means of an excess of iron sulphide, carried out with such a quantity of FeS and such an excess of ammonium sulphide as will produce practically only soluble ferrocyanide; (2) The re-use of the iron sulphide from previous in subsequent operations. The inventors who have previously been working at the problem of extracting cyanogen compounds from crude coal-gas have been chiefly trying to obtain insoluble ferrocyanides (which causes complications) or sulphocyanides, the value of which is much less than that of the ferrocyanides. Carpenter and Linder have proved (*Reports on Alkali, etc., Works, supra*, p. 1311) that the crude gas contains cyanogen only as hydrocyanic acid or ammonium cyanide; in the absence of air all the cyanogen in the ammonia liquors is present as ammonium cyanide, and whatever ferrocyanide and sulphocyanide is found, is due to secondary action. The cyanogen may be altogether transformed into these products by suitable treatment, and it is most profitable to aim at the production of soluble ammonium ferrocyanide, on account of its greater value. This might be done by agitation with ferrous oxide or carbonate, but this process has certain drawbacks, especially a loss in the shape of insoluble double compounds. This is avoided by employing ferrous sulphide in the presence of a sufficient excess of ammonium sulphide. The ferrous sulphide must be employed at first in great excess, since the quantity of cyanogen compounds in ammonia liquors varies considerably, but the FeS not converted into ferrocyanide remains behind in an insoluble form and is turned to use in the next operation, where there is a sufficient excess of ammonium sulphide. The iron removed in the shape of ferrocyanide is replaced by ferrous chloride, which is more convenient to use than ferrous sulphide, and which is at once converted into FeS by the NH_4S.

It is best to work continuously in a properly constructed washer, to regulate the addition of ferrous sulphide and chloride so as to ensure the proper quantity of iron compounds being at all times present, to collect the settlings in a store tank, and to determine by tests the quantity required for the conversion of the ammonium cyanide in the next batch of ammonia liquor. The crude liquor should be used as fresh as possible, but it should be well settled and free from tar. After treatment as above and settling again, it is passed through the ammonia-still in the same manner as at present. The effluent from the still will contain more ferrocyanide and less sulphocyanide than hitherto. It is settled in the usual way and the ferrocyanide is precipitated by ferrous or ferric chloride, in the shape of Prussian blue, which can be easily converted into marketable sodium ferrocyanide. The effluent still remaining should be dealt with as described in a later section of this chapter.

Grossmann points out that, according to Carpenter's and Linder's investigations, in the distillation of crude ammonia liquors, hydrocyanic acid is evolved, and therefore the vapours and condensation products are highly poisonous. This would be completely remedied by the conversion of ammonium cyanide into ferrocyanide. The average quantity of sodium ferrocyanide obtainable per ton of coal carbonized amounts in coke-ovens to about 1·1 lb. and in gas-works to about 1·6 lb. The cost of chemicals and working expenses is about 1d. per lb. of ferrocyanide, leaving a clear margin of about 2¾d. per ton of coal in coke-works, and over 4d. per ton of coal in gas-works.

Removal of the Tar-fog from the Gases before treating them for Ammonia.

This is very important for obtaining good products.

Dr C. Otto & Co. (Ger. Ps. 203254 and 204576) remove the tar fog from the hot gases of destructive distillation by means of a tar-spray jet, which at the same time produces the forward movement of the gases. These can then be immediately passed into the acid intended for absorbing the ammonia. A jet of thin tar is introduced into the gas previously to the tar-spray blower, which process has the advantage of washing any lumps of tar retained in the thick-tar blower out of the latter.

Purves, in *J. Soc. Chem. Ind.*, 1915, p. 335, commends this process as "easily the best" for the purpose in question.

Burstell (B. Ps. 10901, 1908) describes a washer or cooler for the purpose of depriving gases of tar and dust, and for cooling the gas.

The Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft (Fr. P. 461956) removes the tar from warm gases by introducing the gas beneath a flat plate with holes of 1 cm. diameter and immersed in a layer of tar or tar-oil, so that large bubbles of the gas rise in a steady stream through the tar, the surface of which remains comparatively calm. Owing to surface tension, the bubbles become flattened as they reach the surface, and the tar, etc., contained in the gas is effectively removed as the bubbles escape from the surface.

MANUFACTURE OF AMMONIACAL COMPOUNDS BY DISTILLING THE LIQUOR.

Question of Boiling with or without Lime (Volatile and Fixed Ammonia).

Much of the ammonia in ammoniacal-liquor (in good liquor most of it) is present in the form of salts which volatilize on boiling, and thereby suffer dissociation—essentially ammonium carbonate and sulphide. This "volatile" ammonia can be expelled by simple prolonged boiling of the liquor; but the "fixed" ammonia—that is, that which is present as sulphate chloride, culphocyanide, etc.—remains behind, and can only be expelled by *decomposing the salts with lime.*

We have seen (pp. 1257 *et seq.*) that the proportion between "volatile" and "fixed" ammonia varies greatly. In very good liquors only a small percentage of the ammonia is "fixed"; and in such cases the treatment with lime, which complicates the apparatus and process and greatly prolongs the boiling, does not seem to pay. Hence many manufacturers never use any lime in their ammonia-stills (according to *Dr Ballard's Report*, p. 129, only a minority of English ammonia-makers do so).

The use of lime, however, ought never to be omitted if the "fixed" ammonia exceeds a very few per cent. of the total ammonia. Although even by the lime treatment the latter is rarely absolutely set free and utilized, yet the additional ammonia gained by its use pays very well for the process if it amounts to at least something like 5 per cent.; and this is probably the general case with gas-liquors mixed from all parts of the condensing- and scrubbing-plant.

J. H. Cox (*cf.* p. 1260) considers it a good rule to add 50 lb. of lime per 1000 gall. for every 100 grains of fixed ammonia per gallon of the liquor, that is, 350 lime to 100 fixed ammonia. In practice it is easy, by analyzing the products of manufacture, to find out the proper quantity of lime to add, which, of course, is always greatly in excess of the theoretical.

In an apparatus consisting of two stills (in the second of which lime was used), J. Hepworth (*J. Gas Lighting*, October 1883) found the following strengths of liquor:—

As run into No. 1 still . . .	2·540	per cent. NH_3.
" " No. 2 still . . .	0·589	" "
As taken from No. 2 still . . .	0·068	" "

The difference between the two latter tests represents the "fixed" ammonia recovered by lime.

According to the general experience of German gas-works, the fixed ammonia on an average amounts to one-fifth of the total ammonia.

In any case, all apparatus are so contrived that first the volatile ammonium salts are expelled by heat alone, before lime is added to decompose the fixed salts—at any rate, when the production of sulphate is aimed at. Since in all practical cases an excess of lime must be employed, there is always some trouble from *crusts* of calcium hydrate, and even of calcium salts, firmly adhering to the bottom and sides of the still. This is especially awkward in the case of stills heated by direct fire, and is probably the principal cause why so many sulphate manufacturers forego the recovery of the fixed ammonia; but that drawback may be said to have been entirely overcome by the stills of Grüneberg, Feldmann, P. Mallet, and other modern inventions to be described later on.

It is generally assumed that when an ammonium salt (say ammonium chloride) and calcium hydrate meet, ammonia is immediately set free and calcium chloride is formed. This is contradicted by Isambert (*Comptes rend.*, c., p. 857), who argues that the reaction

$$2HN_4Cl + CaO = CaCl_2 + 2NH_3 + H_2O$$

absorbs heat to the amount of 10·9 cals.; if the lime is used in the caustic state, 7·55 cals. should be deducted for the previous formation of $Ca(OH)_2$. Hence at "ordinary" temperatures no ammonia is set free, even *in vacuo;* but the compound $CaCl_2(NH_3)_2$ is produced, in the formation of which 14 cals. are evolved, and which gives off its ammonia at 180° to 200°. This is also the case with baryta and strontia, but not with lead oxide.

Without entering upon a discussion as to the validity of these theoretical considerations, it must be stated that a considerable amount of boiling is certainly necessary to expel all the ammonia from the above mixture, that this can be done only by prolonged treatment in the hot state, and that it is much better effected in dilute than in concentrated liquors. Usually the treatment in practical working is not continued up to the point where all ammonia is expelled. Cox (*cf.* p. 1260) states that at the works he managed the liquor contained 15 per cent. of its total ammonia combined as fixed salt, and that by the lime treatment 5 per cent. of this was recovered, 10 per cent. going to waste; but this is decidedly far more than need be lost. At the same meeting, Hepworth quoted his own case, in which, of the total ammonia, 76·9 per cent. was expelled by boiling alone, 20·5 by treatment with lime, and only 2·6 remained in the waste liquor; and even this (apparent) final loss would probably in reality be less, as caustic soda had been employed for testing, by which some of the cyanides were decomposed. At most German works, also, the loss of ammonia in the waste liquors is quite insignificant. The best proof that Mr Cox's figures do not represent by far the ordinary state of the case is afforded by the daily practice of all ammonia-soda works, whose ammonia is mostly "fixed," and which could not economically exist if they lost anything like that amount of NH_3 in their waste liquors.

Sometimes the distillation with lime causes a very awkward frothing. This, according to the Société anonyme des produits chimiques du Sud-Ouest (Ger. 18773), is caused by calcium carbonate in a state of suspension. It is therefore proposed by that firm first to drive off the volatile ammonia, and then slightly to acidulate the liquor before adding lime.

Spencer and Sisson (B. P. 92, 1893) slake the lime with hot waste-liquor from the stills, in order to economize heat, to save the lime present in the liquor, and to diminish its volume.

Preparation of the Milk-of-Lime.

The slaking of the lime and the conversion of the slaked lime into a milk are generally known operations. Where it is to be done on a very large scale, the apparatus used for preparing the very large quantities of milk-of-lime required for the Weldon manganese recovery process may be used. This is shown in Figs. 255 and 256. Two cylindrical iron tanks, I and K, are placed one above the other. They are generally about 6 to 8 ft. wide, and of the same height. I serves for slaking the lime and preparing the milk, K for storing the latter as a reservoir for the pump. A donkey-engine, *a*, bolted to I, drives the agitating-gear for both cylinders. In I there is a cage, *b*, formed of perforated metal plates, into which the quicklime is put; it occupies a segment of an annular space in the upper third of I, one-third or half round its circumference; the upper cross-arm of the agitator is accordingly shortened. The milk-of-lime runs from I through tap *c* on to the perforated zinc plate in the sieve *d*, and from this into K.

A steam pump, by means of which the exact quantity of milk-of-lime required for liberating the ammonia is supplied to the still in small quantities and in regular intervals, has been patented by the Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft, Ger. P. 124134.

Hartmann (Ger. P. 164723) also describes a pump for both agitating and pumping the milk-of-lime for ammonia-stills.

C. Menzel Söhne (Ger. P. 165098) describe an apparatus for the automatic distribution of the milk-of-lime on several stills in a given order, consisting of several chambers with taps and overflows.

Peters (*J. Gasbeleucht.*, xlix., p. 163) describes arrangements for the automatic supply of lime-milk to ammonia-stills, and for preventing losses of ammonia from these.

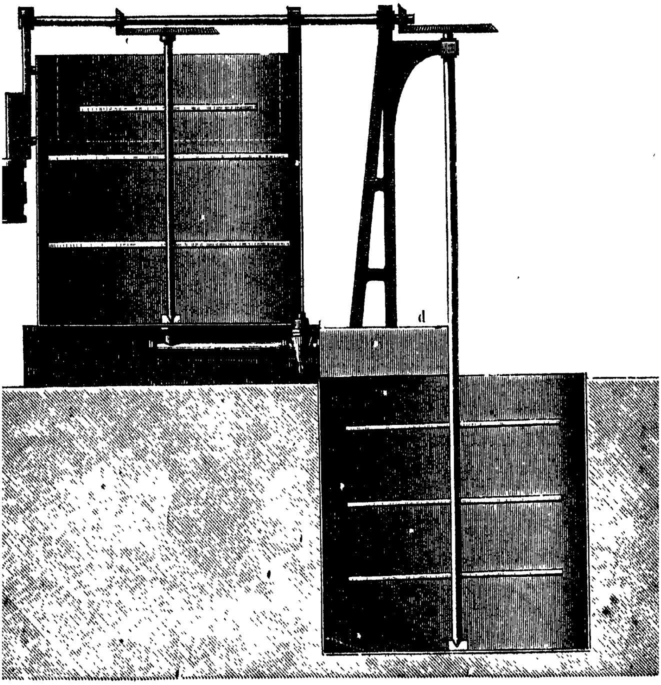

FIG. 256.

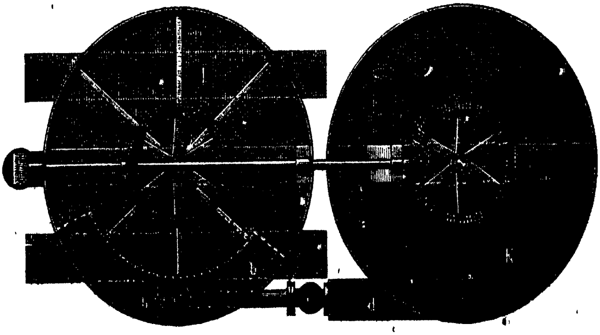

FIG. 257.

The milk-of-lime should not be either too highly or too little concentrated. On one side, the stills ought not to be weighted with driving off too much water; on the other side, the milk-of-lime ought not to be so thick that the pump cannot be properly worked. The usual strength is from 15° to 22° Twaddell. It is generally only estimated by the specific gravity of the milk-of-lime. The relation of this to the amount of lime present is shown by a table in Lunge's *Technical Chemists' Handbook*, 1910, p. 157.

The examination of the lime itself, *i.e.* its contents of caustic lime, CaO, is carried out as follows:—A large average sample is broken up to pieces of the size of a bean. 70 g. of these are placed in an enamelled iron dish, containing 750 c.c. of water, which is heated to boiling, the flame being at once removed when the lime begins to slake. After some cooling, the liquid is run into a litre flask and filled up to the mark. Twenty c.c. of the well shaken-up liquid are taken out with a pipette, run into a flask, the pipette is washed into the same, and the liquid at once titrated with standard hydrochloric acid, the indicator being phenolphthaleine, which produces a strong red colour. The cubic centimetres of standard acid used up to the first decoloration is noted; but as the red colour returns again, the titration is continued, adding each time 0·5 c.c. of standard acid, until the solution remains colourless for five minutes. Each cubic centimetre of standard acid indicates 2 per cent. caustic lime, the acid used up to the first decoloration showing the very active lime, that used up to the final change the total caustic lime. The quality of the lime depends upon its percentage of active lime, which goes back if the lime is kept in stock for some time.

Treatment of the Calcium Carbonate Mud.—The Badische Anilin- und Sodafabrik (B. P. 27962, of 1913; Fr. P. 466302) extract any ammonium sulphate contained in that mud by filtering it through "immersion suction filters."

Use of other Compounds for liberating the Ammonia.

Magnesia is sometimes used in lieu of lime for decomposing salts of ammonia; but, apart from analytical purposes, only in such cases when it is intended to recover not merely the ammonia, but also the chlorine of ammonium chloride —a problem belonging to the domain of the manufacture of soda by the ammonia process. It is, of course, an indispensable condition that the magnesia must be recovered, as its price prohibits wasting it like lime. The details of the numerous attempts made in this direction do not belong to the domain of Ammonia Manufacture, but to that of Alkali Manufacture. We will therefore only briefly mention a very important patent of Messrs Péchiney & Co. (B. P. 9927, 1885). They found that the decomposition of solutions of ammonium chloride by magnesia, even at the boiling temperature, is only complete when the liquor is kept in a certain state of concentration, and they have accordingly constructed a still in which no steam is condensed, and no separation of NH_3 and water takes place, till the decomposition has been entirely accomplished. Only then the usual dephlegmation comes into play. *Cf.* p. 1270 as to the greater difficulty caused by magnesia in comparison with lime.

D'Andria (B. P. 5762, 1888), Chatfield (B. P. 6152, 1888), and Naef (Ger. P. 115249) again patent the use of magnesia.

According to the *Alkali Report* for 1891 (No. 28, p. 88), one factory employed *caustic soda* for expelling the fixed ammonia. This is a clean process, but probably too expensive in most cases.

Cerium oxide, or the oxides or oxychlorides of other rare earths are employed by Whitehouse (Ger. P. 202350, of 1907) for obtaining free ammonia, together with chlorine or hydrochloric acid, from ammonium chloride. When heating NH_4Cl and CeO_2 to 100° to 350° C., NH_3 is driven off; the temperature is then raised to 450° to 500°, and steam is injected, whereupon HCl is formed, or else by means of air free chlorine is obtained, $CeOCl_2$ remaining in the latter case. One mol. of $CeOCl_2$ heated with 2 mols. NH_4Cl, yields $CeCl_4$ whereby the cycle of the reactions is established.

Mode of Heating the Stills.

The apparatus for distilling gas-liquor differ in the mode of heating. This may be done either by a direct fire, or by open (wet) steam, or by indirect (dry) steam. Sometimes superheated steam is also employed. Expelling the ammonia by boiling alone, without employing the sensible and latent heat of the vapours evolved, consumes very much time and fuel. Hence in all modern apparatus this heat of the vapours is utilized for a preliminary heating of fresh gas-liquor and for driving out the volatile ammonia, and at the same time the gas is freed from aqueous vapour by dephlegmation. The additional first cost of a properly constructed apparatus is soon repaid by a great saving in fuel. Many kinds of apparatus have been devised for this purpose, a number of which will be described in detail later on; their principle is similar to that employed in rectifying spirit-of-wine or light tar-oils.

Which method of heating is most advantageous for distilling ammonia seems to be decided by the following experiments on a manufacturing scale made by Dr C. M. Tidy. A quantity of gas-liquor, amounting to 7000 gall., requires—

	Hours.	Yields, as compared with the theory.
When heated by open fire from without .	22	90 per cent.
,, ,, indirect steam in a coil .	18	92 ,,
,, ,, open (wet) steam . .	14	98·5 ,,

This proves that steam directly blown into the liquor is by far the best agent, no doubt because its heat is thus most directly utilized, and perhaps even more because the steam mechanically carries away the ammonia.

Safety-valves.

All stills intended for expelling ammonia without lime should be provided with safety-valves—a precaution not unfrequently neglected. The gas-delivery pipes easily get plugged up by ammonium carbonate, and this may lead to dangerous explosions. Seidel (in Hofmann's *Report on the Vienna Exhibition*, i., p. 96) and Watson Smith (private communication) testify to this. This danger is avoided by fitting up the boilers with safety-valves. These are, indeed, nowadays compulsory in German ammonia-works.

Various Products made from Gas-liquor.

These products are:—Concentrated Gas-liquor, Pure Liquor Ammoniæ, Anhydrous Liquid Ammonia, Sulphate of Ammonia, other Ammonium Salts. We now proceed to describe their manufacture.

I. MANUFACTURE OF CONCENTRATED GAS-LIQUOR.

This product, consumed in large quantities in the manufacture of ammonia-soda, is made by a simple distillation of gas-liquor. It is a yellow liquid, smelling strongly of ammonia and sulphide of ammonium, containing 15 or 20 per cent. total NH_3. It serves also for manufacturing other ammonia salts which cannot be equally well prepared from raw gas-liquor, especially on account of the presence of cyanide and sulphocyanide (thiocyanate). At small gas-works this product is preferably made, as requiring little apparatus and no chemicals.

Sometimes two qualities of this liquor are made, viz., either less highly concentrated gas-liquor, containing from 16 to 18 per cent. total NH_3 and comparatively much CO_2 and H_2S, or highly concentrated liquor, containing from 18 to 25 per cent. NH_3 and but little CO_2 and H_2S.

Usually no lime is employed in this operation, but then no product should be aimed at of a higher concentration than the above, to avoid obstruction of the pipes by ammonium carbonate. Of course the fixed ammonia can be subsequently driven out by lime. If stronger liquor than the above is required, lime must be added from the first; the product will then contain mostly free ammonia and ammonium sulphide.

Concentrated gas-liquor, when freshly prepared, is water-white or yellow, and smells of ammonia, pyridine and hydrogen sulphide. On being kept for some time, the colour becomes much darker. It is bought mostly by chemical and manure factories which work it up into other ammonium salts.

An apparatus for producing *moderately concentrated* gas-liquor, which is specially intended for use at small gas-works or tar-works, as it is cheap in respect of first cost and requires hardly any oversight, is supplied by Carl Francke, of Bremen. It contains a still, holding about 400 litres, separated by an internal horizontal diaphragm into an upper and a lower half, communicating by a central pipe. The upper part has an outlet pipe for the vapours; the lower part is surrounded by an iron jacket, in which a fireplace for burning coke is arranged.

The upper part acts like a reflux cooler; the final cooling and condensation of the liquor takes place in an outside, water-cooled worm. This apparatus works with interrupted operations, and furnishes a liquor containing 10 to 12 per cent. NH_3, which is not sufficient for carriage to long distances.

For *higher concentrations* of ammonia, continuously working column-apparatus must be used, which are supplied in various forms by the engineering firms working in that direction. All of these are on the principle of the counter-current between the ammoniacal liquor running in one direction, and steam flowing the opposite way. Such apparatus have been at work for a long time, in the first instance for the manufacture of alcohol, and later on for the rectification of light tar-oils. We have described them in the first part of this treatise, for obtaining benzol from coke-oven gases, etc. (pp. 71 *et seq.*).

C. Still (B. P. 28072, 1912) extracts the ammonia from distillation-gas by cooling the gas by means of cooled liquor and then re-heating it by means of the liquor, which has become heated; the gases are then subjected to a further cooling between the cooling-apparatus and the re-heating apparatus. According to his B. P. 28245, of 1913, part of the cooled gas issuing from the saturator is passed back to the main gas current between the first cooler and the reheater, and this additional gas is first heated by hot crude gas and pre-heated by the hot gas issuing from the separator.

We shall now describe some of the best apparatus for this purpose.

Solvay's Apparatus (Fig. 258)

is specially intended to obtain concentrated crude liquor for ammonia-soda works, up to a strength of 15° per cent. NH_3. It consists of a still, A, divided by partitions C into a number of compartments. Each compartment contains a tank, E, connected with the next compartment at the bottom by a pipe. In the upper part of each compartment is fitted a pipe, T, which is enlarged below and carries the vapours into the liquid of the next tank. The fireplace is at D. The ammoniacal liquor comes from the store-tank K, and goes first into a small vessel, G, in order that the feed may be regulated by means of the valve attached to the lever R and the float X. and enters the

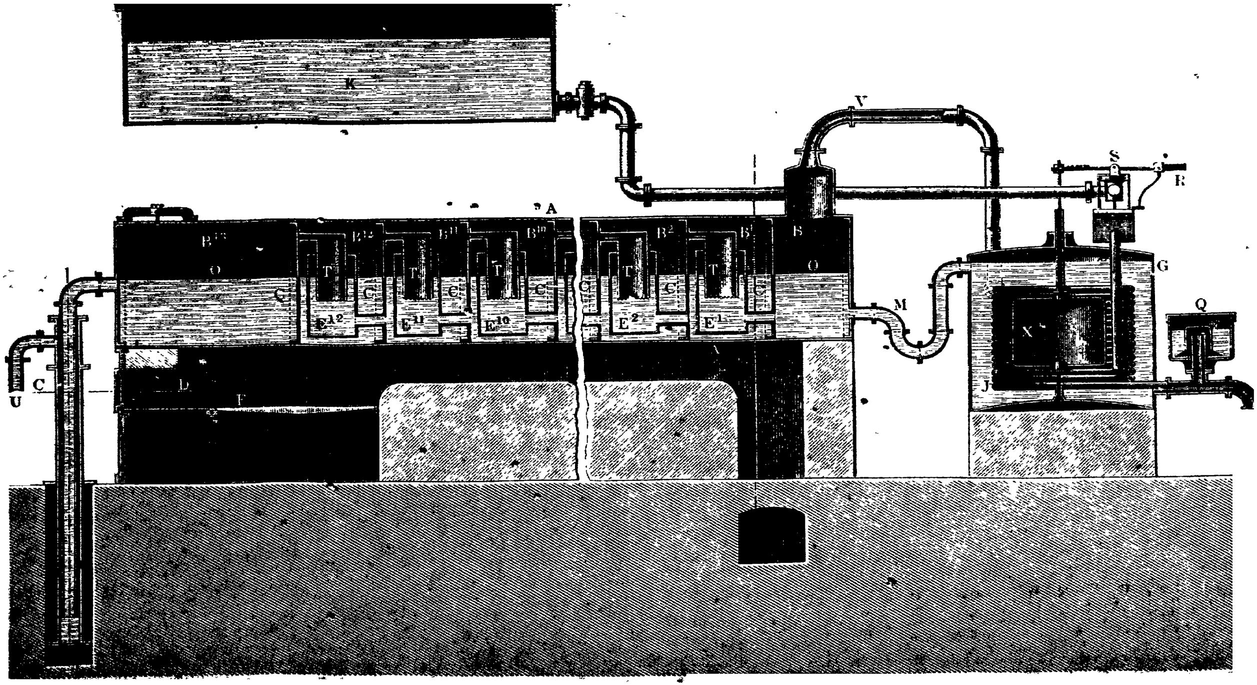
K
V
S
R
A
B^{12}
B^{12}
B^{11}
B^{10}
B^{2}
B^{1}
B
O
O
G
T
T
T
T
T
C
C
C
C
C
C
C
C
M
E^{12}
E^{11}
E^{10}
E^{2}
E^{1}
X
Q
J
C
U
D
F

FIG. 258.

still through the pipe M. Suppose this to be filled equally up to the level O. When vapours are evolved by heating the liquor, *e.g.*, in B^2, they escape by T and force a certain quantity of the liquid into the annular space between T and E^1, and over the edge of E^1 and B^1. Thus a certain quantity of gas-liquor is carried from B^1 to B^2 by means of the vapour evolved in the compartment B^2; in the same way the liquid travels from B^2 to B^3 by means of the vapours evolved there; eventually it arrives in B^{13}, and leaves that compartment by the pipe U. The progress of the liquid principally depends upon the proportion between the diameter of the dipping-pipes T and the vessels E. The vapours arriving in the last chamber B are carried by the pipe V into a worm, J, cooled by ammoniacal liquor, and afterwards through a washing-tank, Q, into the absorbing apparatus. The float X regulates the flow of liquor into the still; it descends as the liquid within the condenser is heated by the evolved vapours, and allows a larger quantity of liquor to enter through the valve S if the distillation goes on more quickly. When the firing is interrupted, no vapours are given off, the liquor ceases to pass from one compartment into another, and the level of the liquid rises; at the same time the float rises, and the valve S ultimately shuts off the feed of liquor entirely. According to Hanrez, the dimensions of the apparatus hitherto constructed are sufficient for concentrating, every twenty-four hours, 12, 24, or 48 cbm. (say tons) of gas-liquor of 2° or 3° Baumé to the above strength, with a consumption of 27 to 36 kg. of fuel per cubic metre. The hot water running away from U can be utilized for a preliminary heating of cold gas-liquor.

Grüneberg's Apparatus for Direct Firing.

H. Grüneberg's older apparatus (Ger. P. 35, of 1877) has been superseded by a different form (Ger. Ps. 5255 and 9392), which alone we shall describe here. One of its principal advantages is that it prevents the lime from forming hard crusts on the heating-surface of the stills, and removes the lime residue without any loss of time. Figs. 259 and 260 are partly elevations, partly sections. An upright cylindrical still, A, heated from the fireplace *w* by flues surrounding it, has within it a vertical cylindrical tube, the bottom of which, extending below the bottom of the boiler, beyond its heating-zone, is closed and furnished with a blow-off cock, *r*, and a perforated screen. The upper end of this tube, reaching nearly to the top of the boiler, is open to the vapour-space in the boiler. Above the boiler is the vessel C, charged with milk-of-lime from the tank G by *e*, and above this a rectifying-column, B, of the kind often employed in spirit-stills. The pipes F F extend from the top of A into the lime-vessel, having near its bottom numerous small perforations. By these

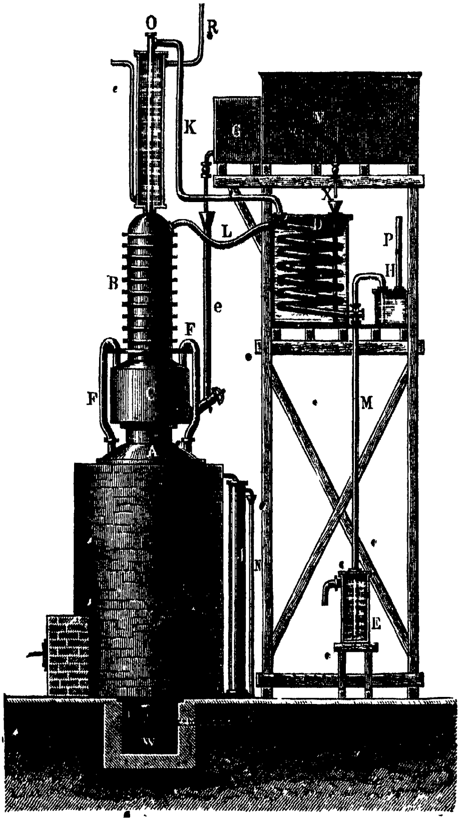

FIG. 259.

pipes the vapours generated in the still are conveyed into the milk-of-lime, and keep this continuously agitated; they then pass through the successive compartments of the column B. This column is supplied by the pipe L with gas-liquor, which descends from one compartment to another, while the vapours ascending from A through C are intimately mixed with it.

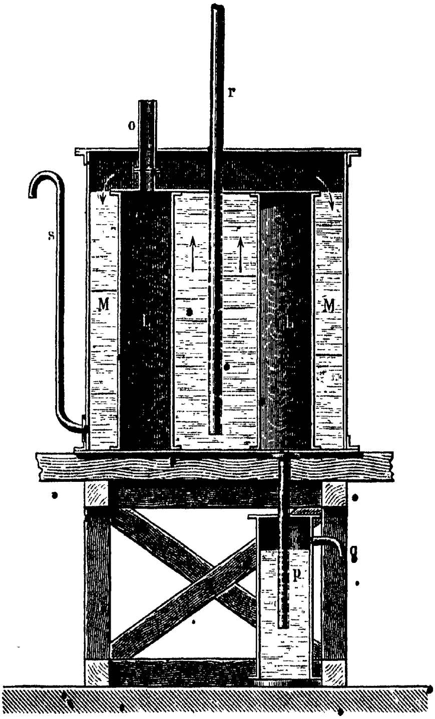

FIG. 260.

Thus the descending gas-liquor is gradually heated and deprived of its volatile ingredients, whilst the ascending vapours are partly condensed and mix with the descending liquid; the uncondensed gases, along with those liberated from the liquid in B, pass away through the pipe K. From the bottom of B the liquid, still containing the non-volatile ammonium salts, flows through an opening into the lime-vessel C and is mixed with its contents, the vapours from F F producing a continuous agitation. Here the ammonium salts are decomposed, and part of the ammonia passes along through B into K. The liquid, still containing ammonia, passes, by the overflow-pipes F, to the bottom of the boiler-tube, which is removed from the direct action of the fire, so that there is no danger of the lime becoming attached to the surface of the tube, neither can the material of the tube, or that of the lime-vessel, be injured by overheating.

From the bottom of the tube the liquid rises through the perforated plate, flows over into the outer boiler A, and is there heated; the gases and vapours evolved are conveyed by F F into C, as above mentioned. From the bottom of A the liquid, now entirely deprived of ammonia, overflows into a deep vessel, J, the contents of which operate as a hydraulic seal, and from this through N to a drain. All this proceeds *continuously*—the feeding with gas-liquor by L, the overflowing of the spent liquor by N, and the escape of the ammoniacal vapours at K.

The apparatus Fig. 259 serves for producing a concentrated solution of ammonium carbonate and sulphide, *e.g.*, for the ammoniacal-soda process. The vapours rise through the cooling-pipe O into a worm in the vessel D, where they are condensed to the condition of (impure) liquor ammoniæ. This flows into a vessel, E, whilst the uncondensed vapours and gas pass into a vessel, H, whose contents form a hydraulic seal. The gas not condensed here escapes through P. The vessel D is closed; and the worm within is cooled by raw gas-liquor supplied from the reservoir V by the funnel-pipe X; after getting heated here, it passes through L into the column B. The cooling-pipe O acts as a regulator of the concentration. The more cold water is supplied to its casing by the pipe R, the greater is the condensation of aqueous vapour in O, the condensed water flowing back into B, and the more concentrated is the residual fluid which passes to the worm in D. Thus the degree of concentration of the liquid ammonia can be regulated at will.

If it were intended to make commercial liquor ammoniæ, the vapours issuing from the column would have to be passed through a number of vessels filled with milk-of-lime in order to retain CO_2 and H_2S, and finally into a cooled absorbing vessel.

The worm D in Fig. 259, which is sometimes stopped up by crystallizations of ammonium carbonate, was later on replaced by a cooler, acting both inside and outside, as shown in Fig. 260. L is an annular iron vessel, fixed in the outer cylinder M. The ammoniacal vapours enter at *o*, condense in L, and the condensing-liquor runs off at *p* into a hydraulic seal, whence it runs over at *q* into the vessels intended to carry it away. The cooling-water enters at the bottom of the vessel, runs over the annular cooler L, and is carried off from this by another tube.

Grüneberg and Blum's Steam-still.

This apparatus (Ger. P. 33320, of the Berlin-Anhaltische Maschinenbau-Ak.-Ges.) contains a cylindrical iron vessel, forming a reflux-cooler, the upper part being kept full of water, the lower part containing gas-liquor. The ammonia vapours, partly cooled here, are completely condensed by means of an iron worm as concentrated gas-liquor, and collected in a receiver. For each 100 kg. concentrated gas-liquor of 17 per cent. NH_3, 2·3 tons cooling-water of 13° C. is required. This still has also been superseded by more modern constructions. So has also Ger. P. 64367, both of them shown in our former editions.

The Apparatus of the Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft.[1]

This firm supplies apparatus of their own construction for all the branches of the manufacture of ammoniacal compounds.

Fig. 261 shows their *still for crude ammoniacal liquor.*

It consists of a number of cells, combined to a column, each cell being provided with steam pipes, covered by dishes nicked at the bottom, and with an overflow for the liquor; also with a cleaning-hole. They are accessible in all their parts, so that the apparatus can be cleaned out without dismantling it. The preheated ammoniacal liquor enters into the top cell, the fresh steam at the bottom, so that it is compelled by the dishes to bubble through the liquor. The crude liquor is gradually heated to boiling, and yields its volatile ammonia, together with other gases, to the steam in the upper half of the column. In a special larger cell, visible about midway down the column, a more vivid motion is produced by means of the dishes dipping lower down in the liquor; here the milk-of-lime, required for liberating the combined ammonia, is introduced in slight excess and mixed with the liquor. The ammonia, thus set free, is driven out by further boiling in the lower half of the column. The spent liquor, which contains but 0.005 per cent. NH_3, leaves the apparatus by an automatically regulated outlet-valve, and can be usefully employed for pre-heating fresh liquor, as its temperature is about 100° C. The outlet-valve consists of

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[1] This long title is practically abridged, by combining the initials, to the trade-mark "Bamag," used for all the apparatus of this factory, which are protected by numerous patents.

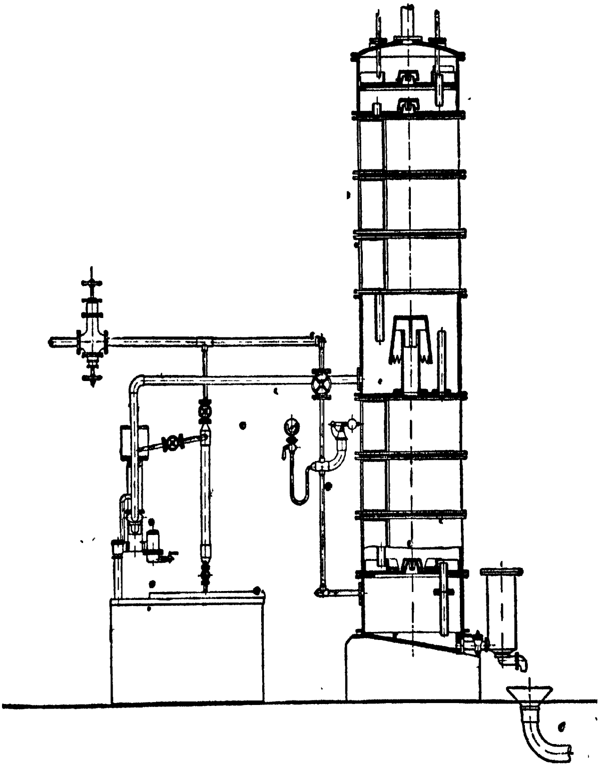


FIG. 261.

a movable float of lead-coated sheet-iron, carrying the valve-cone on an iron rod. The float is placed in a cast-iron box, and is under the same steam-pressure as the lower part of the column, so that the depth of water at which the valve opens always remains the same. The steam-inlet pipe bears a pressure-gauge, a steam-inlet valve, and a safety-valve. The steam-pressure during the work is only from 0·1 to 0·3 atmospheres; the safety-valve blows off at 0·4 to 0·5 atmospheres.

The pre-heating of the crude liquor takes place in tubular apparatus, Fig. 262, in which the hot-spent liquor descends in the tubes, while the crude liquor rises around them, and leaves the apparatus at a temperature of 70° to 80° C.

Fig. 263 shows the regulator for supplying the crude-liquor to the column. The supply is kept uniform by a regulator, and is measured by a tumbling-box, the movements of which are transferred to an index, showing the consumption of liquor in litres on a disk. For larger-sized apparatus the liquor is measured in a cast-iron piston-meter.

Very small columns may be fed by a hand-pump, but columns of any larger size require a steam-pump. The milk-of-lime may also be introduced in several places, if desired. The pumps require no attendance except oiling and regulating at the outset.

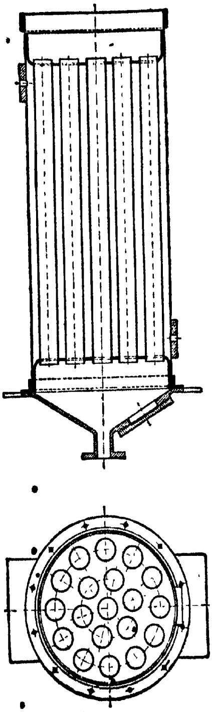


FIG. 262.

An apparatus of the "Bamag" for producing *concentrated ammoniacal liquor* is shown in Fig. 265. Here A denotes a column-still, like that shown in Fig. 261. But since the mixture of steam, ammonia, carbon dioxide, and hydrogen sulphide, which issues at the top, must be deprived of steam to a sufficient extent before being allowed to condense again, it is made to pass through the *reflux-cooler*, B, which is shown on a larger scale in Fig. 266, in which the vapours are partially condensed and enough water is removed from them to furnish a sufficiently strong liquor when being completely cooled in the cell-cooler C. As the water condensed in B contains some NH_3, it goes back into column A.

In case of liquors, testing above 15 to 18 per cent. NH_3, the *carbon dioxide* causes trouble, as the ammonium carbonate is then separated in the shape of solid cakes which frequently stop up the coolers and tanks, and require stoppages and cleaning operations, leading to much loss of ammonia. To prevent this, a special apparatus is interposed for the purpose of removing the carbon dioxide. Up to 15 or 18 per cent. NH_3, this apparatus is not necessary, but such plant is only sufficient for small works. For properly concentrated liquor, testing from 22 to 26 per cent. NH_3, *the* CO_2 *must be removed from the vapours by means of lime.* The apparatus for this purpose, shown at D in Fig. 265, is shown on a larger scale in Fig. 267. This *lime-washer* contains lead-coated plates, placed round a central tube.

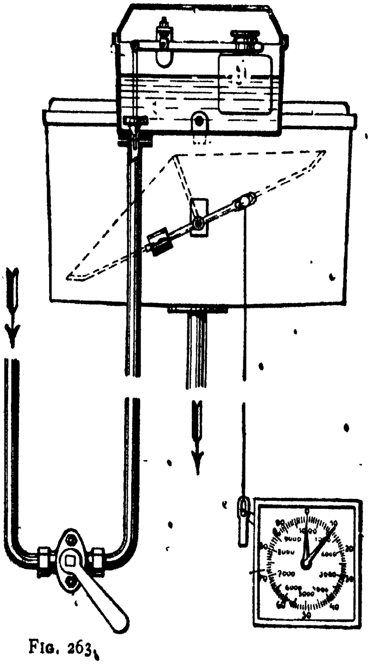


FIG. 263.

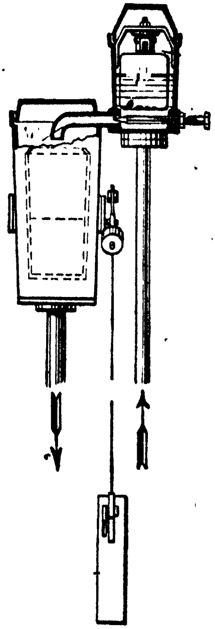


FIG. 264.

Milk-of-lime is pumped in by pump E (Fig. 265) and runs over he plates, being constantly stirred up and carried upwards gain by the gases and vapours passing through the apparatus.

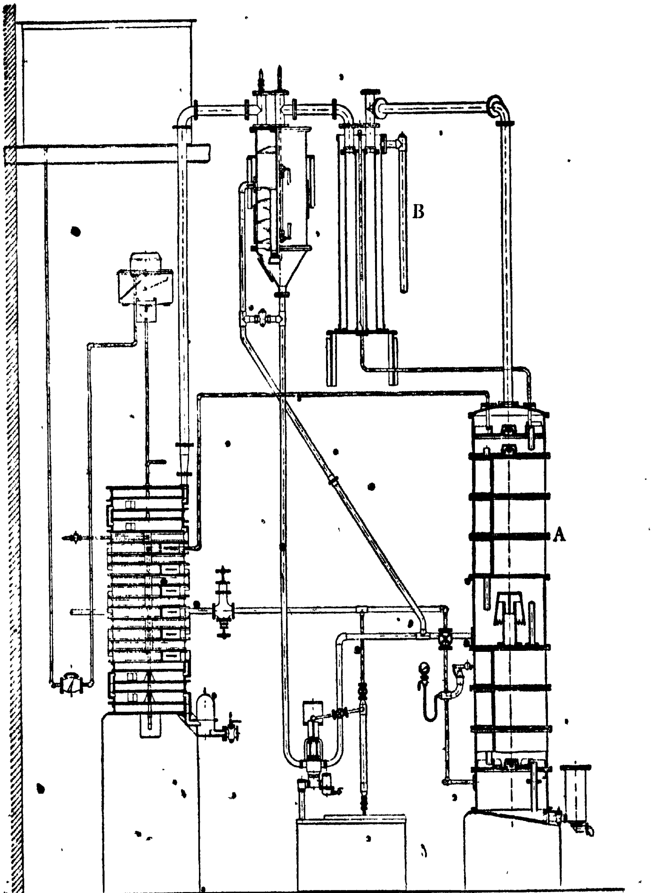


FIG. 265.

The strong agitation of the liquid prevents the deposition of large amounts of calcium carbonate. The used-up milk-of-lime runs automatically back into the still A, where the NH_3 which it has taken up is recovered.

The cell-cooler, shown in Fig. 265, is shown on a larger scale in Fig. 268. It consists of a number of ammonia-cells, *a*, provided with dipping sides, and cooling-cells, *k*, interposed between the ammonia-cells. Each cooling-cell at its top cools the water condensed in the next higher ammonia-cell, and at its bottom, the vapours in the next lower ammonia-cell. The gases and the condensed liquor descend in the apparatus;

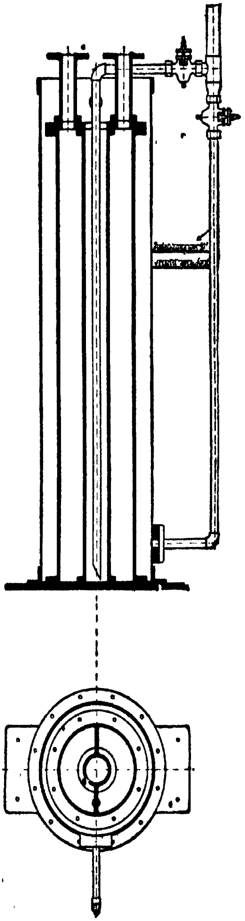


FIG. 266.

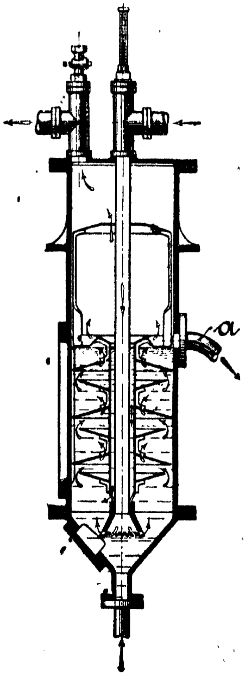


FIG. 267.

the cooling-water taking the opposite direction. At the bottom the concentrated liquor flows into a tank-wagon or other portable vessel.

The "Bamag" also builds plant for manufacturing concen-

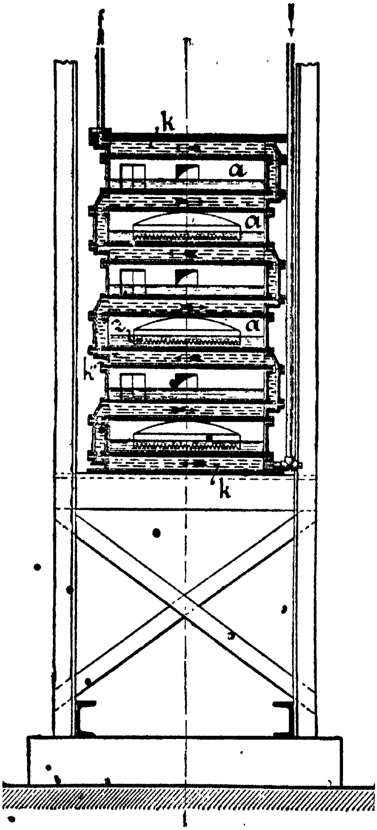


FIG. 268.

trated gas-liquor even in small gas-works; also apparatus in which the CO_2 is driven out by *heat*, founded on the principle that on heating the gas-liquor to 90° or 92° C., about one-half of the CO_2 and one-quarter of the H_2S are given off with very little NH_3. This heating is effected by the waste heat with which the liquor and the ammonia vapours leave the still, thus causing a great saving of steam, lime, and labour. The details of this process are not given in their publications.

According to their Ger. Ps. 204858 and 208254, of 1909, they place the ammonia-still in flues, constructed in the chimney serving for the gas-generating apparatus, especially in cases where there is only one chimney for all of them. This allows small gas-works to work up their liquor without costly apparatus.

Recent Patents of the Bamag.—The Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft (Ger. P. 269658) drive off part of the ammonia by the waste heat of the gas-retorts, and the remainder of the volatile ammonium compounds by stronger heating of the gas-liquor in another vessel. The liquor running away from the latter gives up its heat to an acid-bath and is then run into the water-vessels below the fire-grate of the gas-retorts, in order to be evaporated. Another patent (Ger. P. 272985) states that the stronger heating of the gas-liquor, for the purpose of completely driving off the volatile compounds, takes place in a second or further still, heated by the waste heat of the retort-oven. The Fr. P. is No. 470117; the B. P. 4242 of 1914.

Other apparatus for the manufacture of concentrated ammoniacal liquor is supplied by Julius Pintsch, Aktien-Gesellschaft, Berlin.

The Bergwerksgesellschaft Trier, at Hamm (Ger. P. 286606), employ for the heating of the liquor a vessel made of quartz, which is not acted upon by the liquor, like copper or lead vessels.

The manufacture of concentrated ammoniacal gas-liquor is described in detail by Hilgenstock, in *J. Gasbeleucht.*, 1915, pp. 115 *et seq.*, without any new matter.

The Apparatus employed in Ammonia-Soda Works

is not described here, but reference is made to the author's *Sulphuric Acid and Alkali*, vol. iii., where full details are given respecting its use in alkali-works.

Special Processes for treating Ammoniacal Liquor.

Bonneau and Hasenfratz (Fr. P. 468535 and additions; *J. Soc. Chem. Ind.*, 1914, p. 962, and 1915, p. 283) distil the gas-liquor and extract the sulphur from the residue by a volatile solvent, preferably trichloroethylene, in an apparatus described in Bonneau's Fr. P. 457905. The resulting solution of ammonium salts is distilled with lime, and then treated with lime and water, whereby Prussian blue is converted into soluble calcium ferrocyanide. Potassium chloride is added to the ferrocyanide solution to precipitate the double ferrocyanide of calcium and potassium, and this is converted by sodium carbonate into potassium-sodium ferrocyanide which is treated with a ferric salt to obtain pure Prussian blue.

Chur (Ger. P. 277379) brings the gases from dry distillation, cooled and freed from tar, into contact with warm concentrated ammoniacal liquor so that before flowing to the separator it is enriched with ammonia and warmed. In order to produce the warm concentrated ammoniacal liquor, the gas-water is passed through a boiler provided with a reflux condenser and an apparatus to drive off the ammonia, which is returned to the boiler and then is passed into a vessel the contents of which are in continuous circulation with the distillation gases.

Fillunger (Ger. P. 209847; Austr. P. 27071) distils the gas-liquor without lime; the residual liquor, after cooling, is again passed through the gas-washers and the stills, and this is continued for a long time, so that the formation of large quantities of waste liquor is avoided.

Kremer (Ger. P. 157980) injects hot air into the still, in order to break up the drops of liquor and to enlarge the heating-surface.

Carr (B. P. 16978, 1898) employs a number of pipes, one above the other, and superheats the vapours, in order to convert the cyanides into ammonia.

Carpenter (B. P. 22518, 1906) describes some modifications of the ammonia stills. So does Unger (*J. Gas Lighting*, cxxxii., p. 144; *J. Soc. Chem. Ind.*, 1915, p. 1079).

Concluding Remarks.

The prevention of nuisance during these operations will be described in connection with the apparatus for the manufacture of sulphate.

The *testing* of concentrated gas-liquor is effected in the same way as that of crude liquor, *supra*, pp. 1266 *et seq.* Sometimes it is performed by simply boiling the liquor, diluted with ten times its bulk of water, with an excess of standard acid and re-titrating with standard soda.

II. MANUFACTURE OF PURE LIQUOR AMMONIÆ.

This is the most difficult, but the most remunerative way of dealing with gas-liquor, and is practised on a very large scale, the demand for this article for cold-producing machines being very great.

Liquor ammoniæ is a more or less pure and concentrated solution of caustic ammonia in water. Beside ammonia it frequently contains compound organic bases and other tarry products, which impart to it a disagreeable smell, and sometimes also a yellow or brownish colour. This yellow (amber) colour is often not present in the freshly prepared liquor, but is developed from the empyreumatic substances in course of time, especially under the influence of sunlight. The liquor ammoniæ derived from sewage, directly or indirectly, contains hardly any of these impurities, while that derived from gas-liquor is sometimes very much contaminated by them.

Formerly liquor ammoniæ was prepared by distilling sal-ammoniac with slaked lime; and for analytical purposes this is still sometimes done, but even then only exceptionally, since the ammonium sulphate is very much cheaper than the chloride. When employing sulphate, it is usual to carry on the operation in a cast-iron still provided with an agitator, to prevent a crust of calcium sulphate from impeding the further reaction of the lime upon the ammonium salt. Even from sulphate very little caustic ammonia is now made, since it is easy to make it directly from gas-liquor, by one or two distillations.

When making liquor ammoniæ directly from gas-liquor or any other ammoniacal liquor containing principally ammonium carbonate and sulphide, sufficient *lime* must be added from the outset to retain the carbon dioxide and hydrogen sulphide. According to Francke, the results obtained in a number of works have shown that in the manufacture of liquor ammoniæ from three to three and a half times as much lime must be used as is required for the manufacture of ammonium sulphate.

The consumption of *steam* for the manufacture of liquor ammoniæ is also greater than that required for concentrated ammoniacal liquor or ammonium sulphate, because part of the steam is required for preparing distilled water for the absorption of the ammonia. For this purpose a cooler and a collecting-tank for distilled water must be placed at such a height that the water can be run straight into the absorbing-vessels.

Before the absorption, the ammonia gas must be *purified* as much as possible from steam, and from carbon dioxide, hydrogen sulphide, organic bases and empyreumatic substances. Most of the steam is retained by the reflux-cooler; that quantity of steam which corresponds to the tension of aqueous vapour at the temperature of the gas leaving that cooler is retained, if necessary, by other means, *e.g.*, a column filled with caustic lime, etc.

Removal of Hydrogen Sulphide and Carbon Dioxide without Lime.

A number of processes for obtaining pure ammonia is based on the fact that on heating crude gas-liquor to about 90° or 95° C., the CO_2 and H_2S split off from the NH_3 and escape, while the NH_3 remains behind in the liquor and can be driven out later on by raising the temperature. We shall describe the more important of these processes, having touched upon some of them *supra*, pp. 1358 *et seq.*

Pfeiffer (*J. Gasbeleucht.*, 1900, p. 89) points out that in the manufacture of liquor ammoniæ the previously heated gas-liquor usually contains two-thirds of the ammonia in the free state, which can be driven off without lime. During the heating up to 100°, mostly H_2S and CO_2 escape, with a little NH_3; these gases are passed through crude gas-liquor, in order to retain the NH_3. The quantity of lime necessary for driving off the fixed ammonia is previously ascertained by the method indicated below; but in order to be on the safe side, about 30 to 50 per cent. more lime is slaked to cream and is pumped into the gas-liquor, heated as above, after which the distillation is carried on with open steam. The ammonia-gas, containing aqueous vapour together with a little H_2S, CO_2, and empyreuma, has to pass three milk-of-lime washers, a reflux-cooler, and four charcoal-filters, and is then absorbed in distilled water. The distillation of 3 tons liquor requires eight hours (the heating up to 100° another two hours). The residue in the still contains only 0·03 per cent. NH_3, which it does not pay to recover. The finished liquor ammoniæ never contains any sulphide, even when only the theoretical quantity of lime has been employed, and any such contamination can be wholly avoided by interposing (as has been done at the Magdeburg gas-works) between the last charcoal-filter and the absorber a *caustic soda washer*, charged with a 10 per cent. solution of caustic soda. This consists of a cylinder of $\frac{3}{16}$-in. sheet-iron, 2 ft. 8 in. wide, 2 ft. 3 in. high, with an inside bell, 2 ft. 6 in. high, 1 ft. 10 in. wide, perforated in its lower portion (up to 12 in. high) by a number of $\frac{5}{8}$-in. holes. The gases pass up the centre, escape through the holes under very slight pressure into the outer space, and away from this to the absorber. The sucking-back of liquid from the latter is prevented by an open water gauge-pipe attached to the washer, about 10 feet high. One filling of this apparatus lasts many months, as it is used only in cases of accident, which are thereby rendered harmless. It also dispenses with the necessity of renewing the lime in the "hot washers," which consequently act only as water-separators.

The whole of the apparatus on Pfeiffer's system employed at the Magdeburg gas-works is described in *J. Gasbeleucht.*, 1903, pp. 1 *et seq.*, and in *J. Soc. Chem. Ind.*, 1903, p. 142.

Pfeiffer's method for ascertaining the quantity of lime required for distillation simply consists in boiling in an open flask 25 or 50 c.c. of raw (or 100 c.c. of previously heated) gas-liquor with 20 c.c. of a milk-of-lime containing 2·8 g. CaO, after diluting to 200 c.c., until all the ammonia is expelled (which takes half or three-quarters of an hour after the liquid has been got up to ebullition), cooling down the residue, diluting with water, and titrating back with normal hydrochloric acid and phenolphthalein. Each cubic centimetre of the acid = 0·028 g. CaO; by deducting the CaO still found in the residue, the quantity consumed during the reaction is ascertained.

Solvay & Co. (Ger. P. 49590) remove CO_2 and H_2S by means of a column S (Fig. 269), composed of chambers b to b_4, each of which contains a worm connected outside by the joints w to w_3. Each chamber communicates with the next above by necks d_1 to d_4, covered by hoods e_1 to e_4, and with the next below by overflows f_4 to f_1. The vapours from still A pass through column S into the condenser C, the liquid from this running through *s* into X. C also consists of a number of chambers, *g*, connected by overflows, a worm *i* passing right through. From the bends *w* to w_3 reflux-pipes *z* carry the condensed liquid to a collecting-pipe, *u*, and from this through *v* back into the still. The worm *i* is at the bottom connected by pipe *n* with the gas-liquor tank H. The liquor, heated up in the worm *i* to about 40° C., passes through *o* into washer W, where it takes all the NH_3 out of the vapours escaping from b_4, through *m*, but allows all the CO_2 and H_2S to escape through m_1.

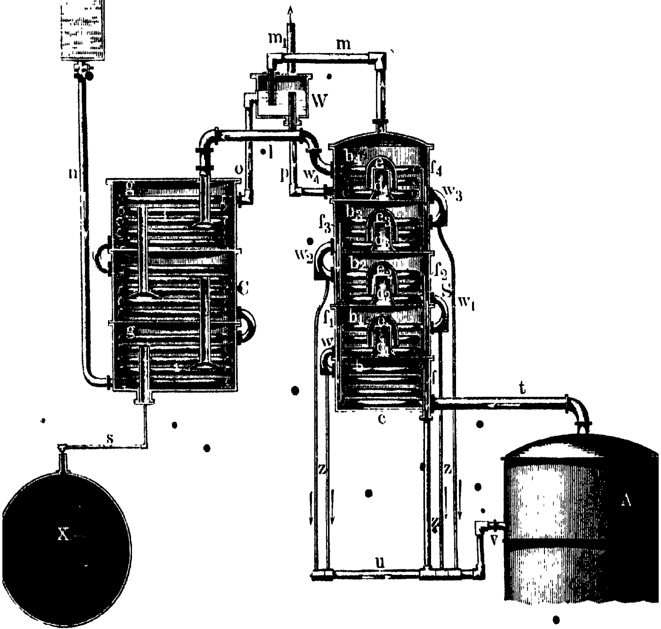


FIG. 269.

Through the descending pipe *p* the liquor runs from washer W into chamber b_4 of the separator, is heated by a steam-coil, passes through overflow f_4 and b_3, and thus gradually through *b*, *f*, *z*, and *v* into still A, getting constantly hotter on its way. CO_2 and H_2S are already given off in b_3 and b_4, and more so in b_2 and b_1, where some ammonia is also set free; which, however, is,

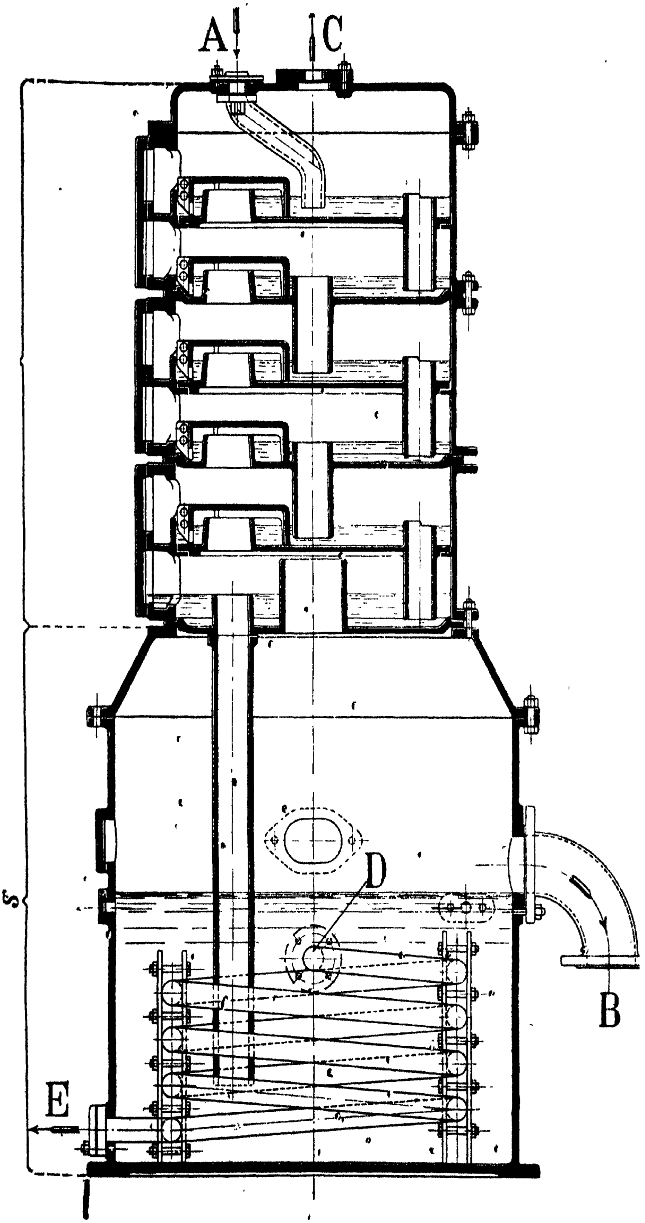


FIG. 270.

retained in the upper, cooler chambers, whilst CO_2 and H_2S escape in the gaseous form. When escaping at *m* they contain but little NH_3, which is retained in W, and in case of need subsequently by a sulphuric-acid washer. The chambers *b* are made of cast-iron, the steam-coils of lead. This apparatus can be employed for making concentrated gas-liquor or else liquor ammoniæ (but the latter certainly not of *pure* quality!).

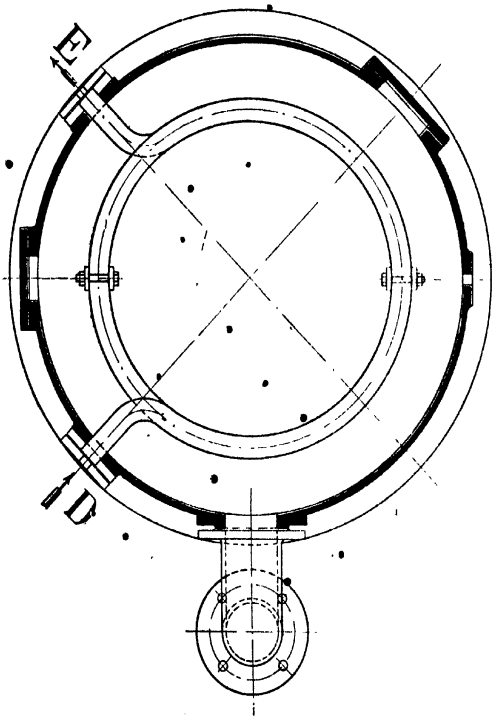


FIG. 271.

Feldmann (B. P. 10501, of 1897) also removes CO_2 and HS_2 without the employment of lime.

The apparatus of the firm, Julius Pintsch Aktien-Gesellschaft, of Berlin, is described in Ger. P. 178030. Figs. 270 to 272 show their apparatus. The lower part of it is a heating-chamber, of which Fig. 271 gives a horizontal section; the upper part is the ammonia-catcher, of which Fig. 272 gives the horizontal section (this is just like their ammonia column-still). In the heating-chamber we see the steam entering at D and passing through a worm, the condensed water issuing at E.

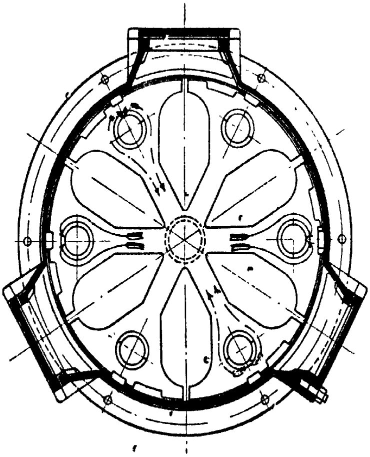


FIG. 272.

The crude gas-liquor runs from the store-tank through the ordinary regulating-apparatus into the top chamber of the ammonia-catcher, descends through it from chamber to chamber, and ultimately nearly to the bottom of the heater, where it is by means of the steam-worm heated up to about 90° C. Here most of the CO_2 and H_2S, with traces of NH_3, are driven off, and rise upwards through the crude liquor flowing downwards. The NH_3 is retained here, the CO_2 and H_2S escape through C. The liquor, deprived of these gases, runs out through B, and is taken to the ammonia still. This apparatus can be also combined with a preheater, utilizing the hot waste liquor of the still for heating up the raw liquor before entering into the heating-chamber.

Purification of the Ammonia Gas from Empyreumatic (tarry) Substances.

When white and pure caustic ammonia is required, the empyreumatic substances must be absorbed in a suitable manner or destroyed. The most usual way of doing this is *filtering* the vapours *through recently ignited wood-charcoal.* In many cases the vapours are also passed through a *fatty oil*, which retains the tarry substances, and can be again partially freed from them by heating. The charcoal absorbs considerable quantities of ammonia (*in maximo* 800 times its volume) which should not be lost, but can be completely recovered by blowing out with steam. For this purpose Francke provides the charcoal filters on one side with a steam-pipe, on the other side with a gas-pipe dipping into the crude-liquor tank where the volatilized ammonia is absorbed. After being steamed, the charcoal is re-activated by heating in a retort. These various apparatus must be provided in duplicate, so that one of them can be put out of function for cleaning. Pfeiffer in one case obtained on steaming the filter 268 kg., in another case 340 kg., liquor ammoniæ of 25 per cent. NH_3.

Watson Smith (private communication) advises in any case, even when liquor ammoniæ is the principal product, to make along with it a little sulphate, because the gas which first and somewhat tempestuously escapes in the distillation carries along with it some tarry matters, and hence is best not employed for making liquor ammoniæ. This procedure cannot be carried out in the continuously acting apparatus to be described below; but even then mostly only crude strong ammoniacal liquor is at first obtained, from which liquor ammoniæ is prepared by distilling into pure water. In order to carry off separately the first evolved portion of ammoniacal gas, the gas-delivery pipe of the ammonia-still is provided with two branches, each of which is shut off by a stopcock, or by a short piece of 2-in. indiarubber pipe with a screw-clamp, so as to direct the vapours either into the ordinary saturating vessel filled with sulphuric acid, or into a worm for condensing crude liquor ammoniæ. The latter is collected in large iron tanks, from which the vapours pass first through a barrel half-filled with water, or preferably, to avoid pressure, through a lead worm, serving as a reflux condenser, in which the vapours ascend and are met by water trickling down from a funnel, to condense the last traces of ammonia. (No doubt a small coke-scrubber fed with water, or preferably with sulphuric acid, would act even more thoroughly.)

Apparatus for the Manufacture of Pure Liquor Ammoniæ.

For this purpose both ordinary stills for interrupted work and column apparatus for continuous manufacture are employed. Where the pure liquor is manufactured at the gas-works from their own crude liquor, the ordinary stills are frequently preferred, but for the manufacture of pure liquor ammoniæ on a large scale it is usual to employ continuously working apparatus, comprising stills of various descriptions, reflux-coolers for condensing most of the steam evolved together with the ammonia, the retention of carbon dioxide and hydrogen sulphide being effected either by applying the requisite amount of lime in the stills, or by dissociation columns, followed by washing with lime; then treating the dry gas with caustic-soda solution, charcoal, and paraffin oil, and ultimately absorbing the purified gas by water. There is a very great variety of apparatus in use for this object, but the principle is always the same, and we may confine ourselves to selecting a few of them for description in this place.

A very simple apparatus, which was in operation at a Manchester works some years ago, is shown in Fig. 273. The liquor is put into a circular still, *a*, 8 ft. long and 4 ft. in diameter, heated by a fire which is kept away from the bottom of the still by an arch, and only circulates round the sides. For every charge of 600 gall., containing 3½ to 4 per cent. ammonia, 2 cwt. of quicklime, previously slaked to a thick paste, is added and a strong fire is made. The gases escape through a 2-in. pipe into a lead worm, *b* (cooled outside by water), in which the aqueous vapour is condensed and flows back. In the descending branch *c* a little water is condensed and collects in the carboys *d*. The nearly dry gas is treated in the purifier *e* (6 ft. long and 4½ ft. wide) with slaked lime, to remove hydrogen sulphide, tar, etc. The top of the purifier is luted with lime-putty and is screwed down tightly; its contents must be renewed two or three times a month. From this the gas passes in a 1-in. pipe through a small washing-arrangement, *f*, and then, by means of indiarubber joints provided with screw-clamps, at will into one of the three absorbers, *g*, *h*, *i*, made of iron lined with lead, 3½ ft. square and 3 ft. high, and provided with gauge-glasses. These vessels are charged with pure water; the gas issues into

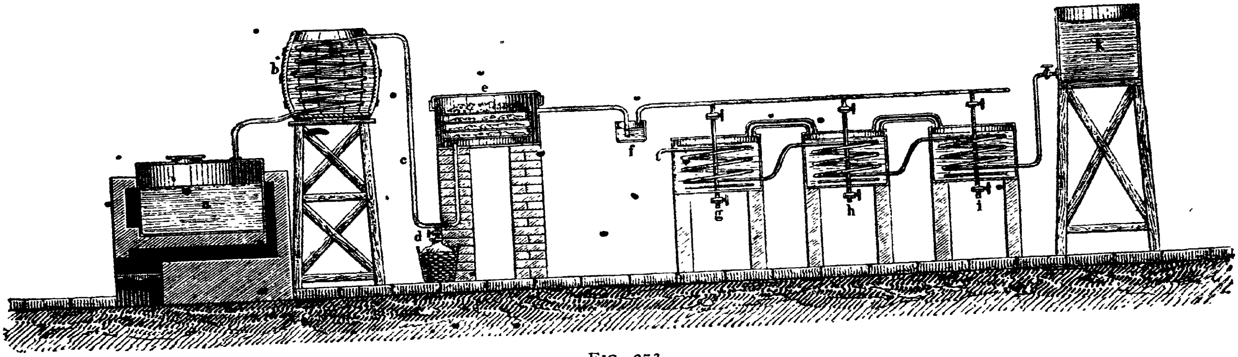


FIG. 273.

them from perforated rings of lead tubing lying at the bottom. These vessels are connected by gas-pipes; they also have an air-vent each, but of course this is only opened in the last one of the series. The contents of *g*, *h*, *i* are cooled by water, which, coming from the tank *k*, is passed through all the absorbers by means of worms. After the liquor has become sufficiently strong, it is drawn off by taps into carboys, ready for sale. It should be clear, free from any greasy matter, and of sp. gr. 0·905, or at most 0·914. No traces of sulphides, indicated by lead acetate or sodium nitrocyanide, should be present. (This description may serve to show how an apparatus can be constructed in a cheap and simple manner; but it lacks some of the qualities of more modern appliances.)

Apparatus of Elvers and Pack.—Fig. 274 is a sketch of this "two-boiler" apparatus for making liquor ammoniæ direct from gas-liquor. We have not reproduced the original sketch, which is somewhat difficult to understand, but placed the parts separately alongside each other, to make the principle clearer. For the same reason all supports, carrying-walls, etc., are left out. A and A′ are cylindrical iron boilers, A′ being placed sideways and above A, which alone is directly heated by the fire. A is surmounted by a dome, to which is attached an air-valve *v*, for avoiding a collapse of the still by the atmospheric pressure on cooling, and the gas-delivery pipe *a*. The latter is carried first up, then down, and enters A′ near the bottom, continuing into a pipe running all along the bottom and perforated with many holes, through which the vapours from A get into A′. The liquid in A′ can be run into A by means of the wide pipe and valve *m*, which can be cleaned from deposit by means of a suitable contrivance. The vapours arising in A′ first ascend in *b*, then descend into the vessel B to within 12 in. of its bottom; the liquid condensed in B runs through *l* into A′ below the level of the liquid there. From B the vapours pass into the worm C, and through *c* into the closed box D. From this the condensed liquid can be run back into A′ by the tap *s* and the pipe *p*. D is provided with a safety-tube, *d*, and a pipe, *e*, for taking away the uncondensed gases. These, now freed from most of the moisture, pass into the four cast-iron pipes E E′ E″ E‴, connected alternately at top and bottom by the pipes *f f′ f″*; they are open at both ends, and closed by plates tightly screwed down. From E''' the gas travels through f'' and g into the leaden absorbing-vessel G, placed in a cold-water tank F; here also a safety-pipe, h, and

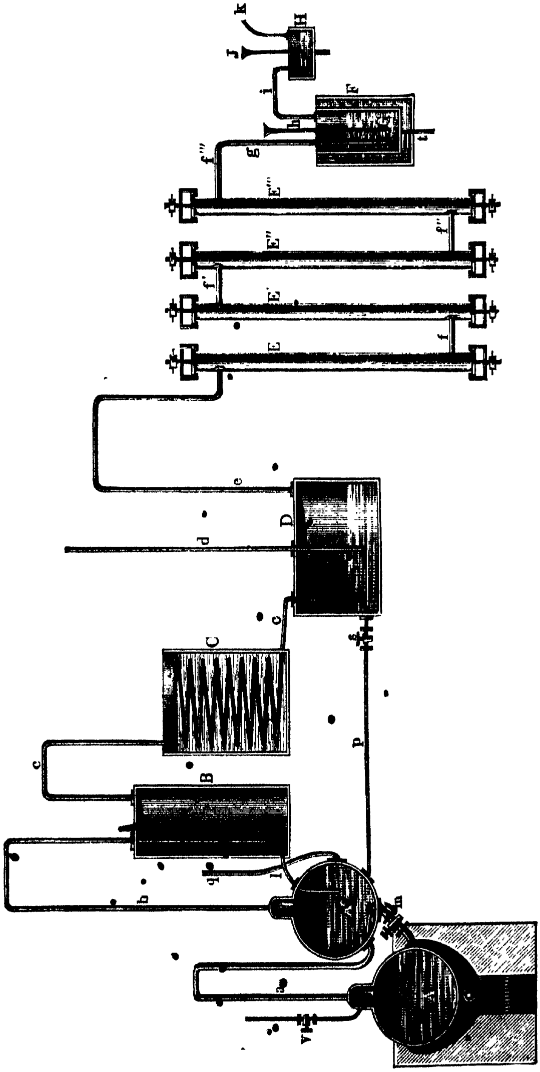


FIG. 274.

a discharge-pipe, *t*, are provided. The residual gas escapes through *i* into a small absorbing-vessel, H, with safety-pipe J; and *k* carries the incondensable gases into the outer air.

First the still A′ is charged by the pipe *q* with about 1000 litres of gas-liquor, contained in a higher store-tank; and this is at once mixed with a sufficient quantity of lime through a special aperture. The valve *m* is opened; the condensers C and F are charged with cold water, the pipes E E′ E″ E‴ with freshly ignited wood-charcoal in pieces the size of a walnut, and the covers are screwed down. G is charged with 60 to 65 litres of water, H with ½ litre. When the liqour mixed with lime has run from A′ through *m* into A, *m* is closed and the fire is lighted. The fire-gases travel along one side of the boiler, return along the other, and then go to the chimney. When the contents of A begin to boil, first the air is expelled and passes in bubbles through the water in G and H; A′ and the pipes are filled with vapours and become heated. Gas-liquor is now run through *q* into A′; by the cooling thus produced, the liquor in D is sucked back into A′ through *c* and *b*, and air enters at *d*. When 1000 litres of gas-liquor nave run into A′, milk-of-lime is again added and well mixed, whereupon the fire is started again. The ammoniacal vapours from A escape through *a* into the liquid in A′, traverse this from the many small holes in the pipes, and give off part of their ammonia to it. A portion of the steam is condensed in B, the water running back into A′ through *l*, along with the volatilized salts. From B the vapours pass into C, where most of the water, together with a portion of the ammonia, is condensed. The condensing liquid serves for washing the ammoniacal vapours, and especially for retaining the salts carried away with them. The uncondensed vapours pass through *e* into the charcoal-purifiers E to E‴, which absorb the impurities mixed with the ammonia-gas. In G the pure ammonia-gas is condensed by cold water, and liquor ammoniæ is obtained. The last remnant of the ammonia is absorbed in H by sulphuric acid; the uncondensable gases escape through *k*. When the still A is worked off, the residue is discharged, and A is recharged from A′. The liquor now re-aspirated from D into A clears the worm C, etc., from any deposit. If in G and H ordinary water, not distilled, has been employed for absorbing the ammonia, the precipitate of calcium, aluminium, and magnesium salts formed must be allowed to settle in order to obtain a clear, marketable product. Each operation takes four or five hours; and from 1000 litres of gas-liquor of 3° Baumé is obtained 100 to 110 kg. of liquor ammoniæ of 32° Baumé (=sp. gr. 0·924).

The Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft ("Bamag") supply the apparatus, shown in Figs. 275 to 278, for the manufacture of pure liquor ammoniæ. The vapours coming from the column-still *a*, provided with automatic outlet valve *q* (*cf.* p. 1352, Fig. 261), are partially cooled in the reflux-cooler *c*, so that only small quantities of water pass over with the ammonia. The remaining gases are completely freed from CO_2 and H_2S by the three carbonic-acid washers *d d d*, constructed as shown in Fig. 267, p. 1356, for concentrated gas-liquor, the milk-of-lime flowing into the last of these at the top, and descending into the second, lastly into that at the bottom; *e* is a "lime-catcher." From here the milk-of-lime is pumped into the column *a*, where the free lime still present decomposes the non-volatile ammonium salts. In *d d d* the CO_2 and H_2S are retained by the lime, and the gases pass through two coolers, *f f*, with the receiver *g*, and a coke-filter, *h*, where the ammonia-gas is further dried and purified. An oil-washer, *i* (*cf.* p. 1367), removes most of the fetid organic substances, and any remaining impurities are retained by the charcoal-washers, h_2 and h_3, from which the ammonia-gas issues in a perfectly pure state. It is retained in the circular, properly cooled absorbers *k*, the last of it in *l*, and furnishes liquor ammonia of any desired strength; *m* is a steam-pump for fresh milk-of-lime, *n* is a pump for pumping the milk-of-lime from the carbonic-acid washers into the still *a*, *o* an apparatus for distilling water, *p* a tank for receiving this, *r* a centrifugal pump for supplying it to the still *a*.

Later on the "Bamag" introduced for the manufacture of liquor ammonia the process of *driving out carbon dioxide by heat* (*cf. supra*, p. 1358), in which the preheated crude liquor is heated up to 92° C., and the remaining CO_2 is saturated by lime in an agitating-vessel, whereupon it passes into the still, and from there the NH_3, which is now in the free state, mixed with steam, and, after previous partial cooling, goes on to the reflux-cooler. The further purification by charcoal, oil, and soda-filter goes on as usual.

The newest patents of the "Bamag" are B. P. 4242, of 1914, and Ger. P. 272985.

Heinrich Hirzel's apparatus (Figs. 279 and 280) produces chemically pure liquor ammoniæ of maximum strength (28° to 30° Baumé). A and A′ are decomposing-vessels, alternately charged with gas-liquor and lime, the mixture being previously made in B. The contents of A and A′ are gradually pumped

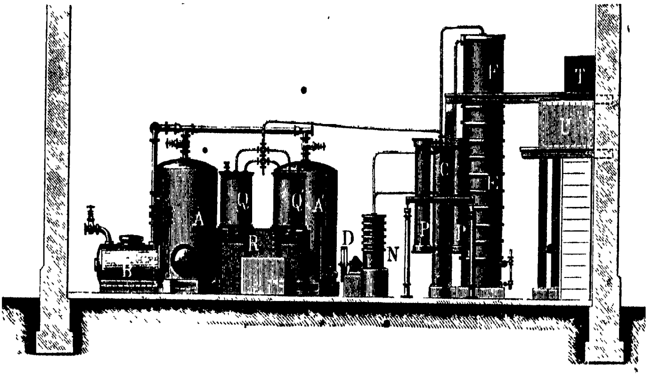


FIG. 279.

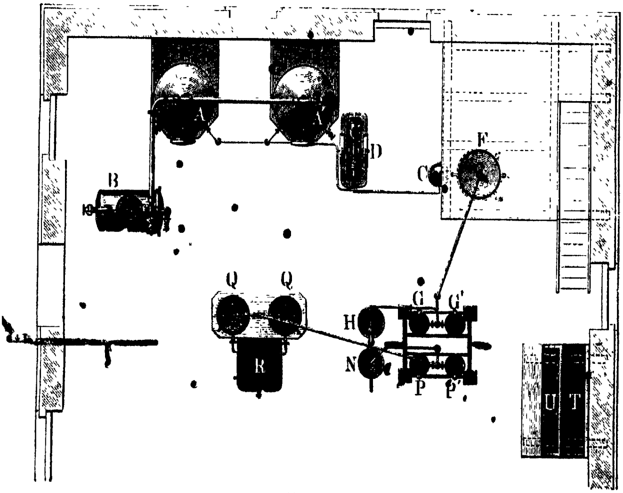


FIG. 280.

by P into the heater F, forming the upper part of column E, into the bottom of which steam is blown. The condenser F dehydrates the gas, which yields its impurities in the washers G, H, N, and P to milk-of-lime, oil, and charcoal; the pure gas passes through P into the cooled absorbers Q and Q′, and from these into receiver R. T serves for preparing distilled water, collected in U, and serving to feed Q and Q′; 97 per cent. of the ammonia can be thus recovered; the waste liquor from the column contains but 0·01 per cent. NH_3.

A new apparatus of Hirzel's (Ger. P. appl. H62171) effects the removal of great part of the carbon dioxide and hydrogen sulphide without the employment of lime, by absorbing the ammonia in fresh water in a special washer, placed near the vessel for removing the carbon dioxide.

Feldmann (B. P. 11711, of 1884) operates in quite a different way. He objects to the employment of lime-washers, etc., after distillation; his principle is, employing a sufficient quantity of lime *before* distillation, and separating the precipitate formed after some time by means of a filter-press. In lieu of the greenish, slimy residues otherwise produced, which are very difficult to dispose of, he obtains, by means of a filter-press, solid cakes, from which the last portions of ammonia are recovered by a washing-arrangement and by excluding the air during the operation. The filtered liquor is now distilled in a column, and the distillate can be brought up to 25 per cent. NH_3, but is still an impure liquor, since the ammonium sulphide is not decomposed by the cold treatment with lime. It is, however, completely decomposed by redistilling with an excess of lime, say, twice the theoretical quantity. As the quantity of liquor is now very small, and the ammonium sulphide on the average is only one-twentieth of the total ammonia, there is no difficulty whatever in that redistillation, especially as the calcium sulphydrate is produced in a liquid form.

P. Mallet recommends his column provided with a mechanical agitator, to be described later on, in connection with the manufacture of sulphate of ammonia, as being particularly adapted for the manufacture of caustic ammonia, where a large excess of lime must be employed.

In order to make colourless liquor, he employs the apparatus shown in Fig. 281. Here A is a cast-iron column, 1 ft. 6

in. wide, formed of 14 chambers containing a solution of caustic soda, introduced by the funnel *a*. B is a similar column, containing a vegetable fatty oil, or heavy mineral oil, for retaining the empyreumatic substances (p. 1367); G, a wrought-iron tubular saturator, through the tubes of which a current of cold water is constantly passing, in order to cool the liquor during the

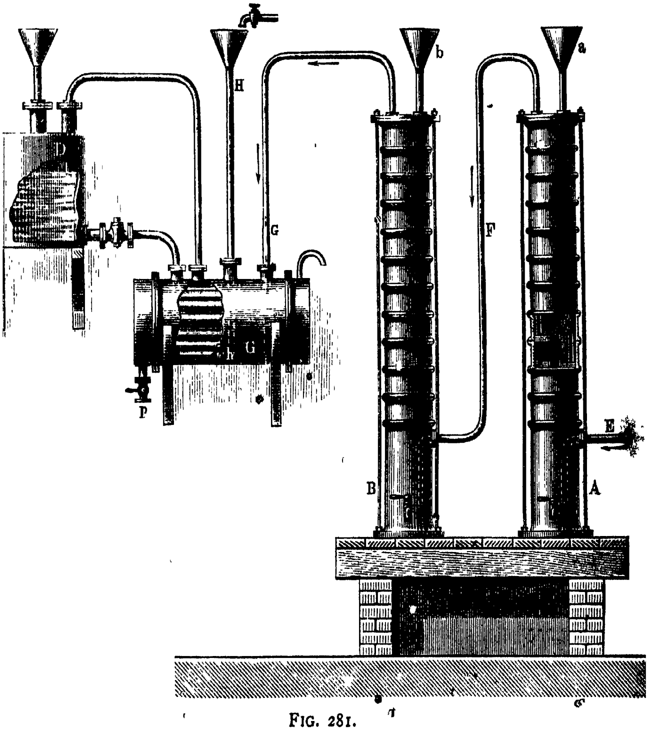


FIG. 281.

condensation of the ammonia; D, a cast-iron safety vessel, in which the gas escaping the action of water in the saturator G is retained. The gas coming from the ammonia-still (where an excess of lime is employed) enters at E into the column A and there parts with most of its impurities, and is completely causticized; in the column B most of the organic alkaloids and empyreumatic substances are retained by the oil; the purified gas meets with cold water in the saturator G; and when the solution is strong enough, it is run off by the tap *p*. The liquor contained in D is now run into G; B is refilled with pure water; and the operation is started again. The liquor ammoniæ thus made keeps colourless even in the sunlight; but it still contains traces of foreign products, as is proved by its being more or less coloured brown by nitric acid. Liquor which is to stand this test as well must be made from sewage liquors.

Improvements to this apparatus are contained in the patents of Mallet and Pagniez (Ger. Ps. 31003 and 66288).

Rousseau (Fr. P., 18th August 1880) recommends that, in rectifying ammonia by dephlegmation, the water should be kept at a temperature of from 60° to 70° C.; below this, *e.g.*, at 55°, the liquor begins to take up ammonia from the gases passing through.

Hegener (Ger. P. 11669) prevents the escape of ammonia in charging with milk-of-lime by means of two tanks placed above the still. In the upper one (R, Fig. 282) the lime is slaked, and the milk-of-lime is let down into the lower one, R′, by the tap H. During this the ammoniacal gases in R are conveyed to a special receiver by a pipe proceeding from the air-tap B. When the milk-of-lime is to be run into the still, the taps H and B are closed, but H′ and the steam-tap D are opened.

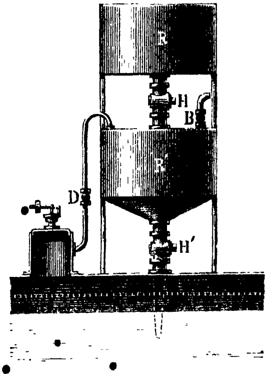


FIG. 282.

An apparatus patented by the Société anonyme des Produits Chimiques du Sud-Ouest (Ger. P. 13429) does not seem to offer any special advantages over those already described.—That of Rube, Engelcke, and Kraus (Ger. P. 15570) consists of a column formed of a number of funnels superposed one over another, into which ammoniacal liquor and milk-of-lime are introduced by separate siphon-pipes.—G. Wunder (Ger. P. 17411) employs the old principle of two boilers, one for the volatile and one for the fixed ammonia, the latter being heated by the steam coming from the former, which itself is heated by a fire.—J. Gareis (Ger. P. 21707; B. P. 3164, of 1882) employs a combination of four vessels, so arranged that the one filled with milk-of-lime is not, like the lowest, heated by a direct fire, but by the steam coming from the latter, just as is done (in a more perfect way) in the Grüneberg stills, p. 1348.—F. Gerold and M. Vacherot (Ger. P. 21821) patent a travelling apparatus for working gas-liquor, consisting of a simple cylindrical boiler, with an inside fire-tube, like a Cornish boiler, resting on a railway truck. [This form of boiler is quite unsuited for distilling gas-water, especially with lime, as proposed by the inventors.]—C. H. Schneider's apparatus (Ger. P. 21252) is a two-boiler still with dephlegmator, without any essential difference in principle from the ordinary apparatus.—The same also applies to the apparatus of C. Berson (B. P. 11449, of 1884), which contains a directly fired retort of peculiar shape. C. Hills (B. P. 5874, of 1884) heats the gas-liquor as it descends in a scrubber, the heat being applied to the lower part of the scrubber. By this means the temperature of the descending stream of gas-liquor is gradually raised, and most of the hydrogen sulphide and carbonic anhydride, and some ammonia, are expelled, the latter being absorbed by the cool gas-liquor in the upper part of the scrubber, whilst the H_2S and CO_2 pass away from the scrubber.

Chur (Ger. P. 166973), in order to purify the NH_3 driven out from gas-liquor from H_2S and CO_2, passes the gas, by means of hydraulically luted bells, through milk-of-lime. In order to compel the gas to remain a long time in contact with the milk-of-lime, without unduly increasing the hydraulic pressure, there is an arrangement of vertical partitions, dividing the space below the bells into a number of chambers through which the gases have to pass in succession.

In a later patent (Ger. P. 188814) Chur places a special decomposing-vessel (lime-mixer) on the top of the distilling-column. In this vessel the preheated concentrated crude gas-liquor is mixed with lime and heated by steam, *without dilution.* Thereby the ammonia is completely split off from the CO_2 and H_2S, and even part of the non-volatile ammonium compounds are decomposed, the remainder being easily decomposed in the column below. Thus the principal quantity of ammonia is already obtained in the lime-mixer, and it is easy to treat there gas-liquor of high percentage, up to 15 to 20 per cent.

NH_3. This takes place because most of the lime is already used-up in the mixer, and the mud, passing through the column along with the gas-liquor, contains lime mostly already neutralized, so that even on working a concentrated liquor the columns do not get obstructed. At the same time the consumption of lime and steam is smaller than usual.

Dr C. Otto & Co. (Ger. P. 174695) employ the liquor from the reflux-cooler for washing the gases to recover any ammonia escaping.

Stine (U.S. P. 929726) produces pure gaseous ammonia by passing air through ammoniacal liquor, which is gradually heated up to 100° and above.

The Société Jules Jean & Cie expels the ammonia from a spray of gas-liquor by means of air.

Frerichs (Ger. P. 222918) prepares pure ammonia from impure gases or volatile ammonium compounds by allowing them to act on ammonium hydrosulphate, which is thereby converted into impure normal ammonium sulphate. This is afterwards heated up to the point that the organic nitrogen compounds are converted into ammonium sulphate. By heating this to 300° to 400° it is transformed into ammonium hydrosulphate, pyrosulphate, and free ammonia; and lastly, the ammonium hydrosulphate obtained in this manner is again exposed to impure ammonia gases. In lieu of ammonium hydrosulphate the hydrosulphates of potassium or sodium may be employed. By this process most of the lime is economized, and the volatile carbon compounds, such as alcohol, benzene, toluene, naphthalene, etc., are removed. The patent shows a suitable apparatus for this purpose.

Maréchal (Fr. P. 350679) removes the sulphur of gas-liquor by means of ozone; the precipitated sulphur is sold in a compressed state.

Hartmann (Ger. P. 164723) describes a pump for both raising and stirring up the milk-of-lime. Two pumps are combined, one of them being connected both ways with the lime-tank and causing a constant circulation of the milk-of-lime; the other pump is connected on the one side with the lime-tank, on the other side with the still, and both are driven by the same mechanism.

Carl Menzel Söhne (Ger. P. 165098) describe a pump for mixing and automatically dividing the milk-of-lime among several stills. An automatic lime-pump is also described by Kordt (*J. Gasbeleucht.*, 1903, p. 375).

Keppich (Ger. P. 125573) separates ammonia from the organic amines present, by passing the mixture of bases, expelled from the still, through a series of absorbers, charged *seriatim* with the equivalent of acid corresponding to each of the bases present, the proportion of which must be previously ascertained by analysis. Thus, he asserts, the bases are separated according to their relative chemical affinity to the acid contained in the absorber.

Coppers (Ger. P. 140350), employs a closed saturator, and allows the steam formed therein to preheat the gas-liquor in a special column from which the main column is fed.

Doersch (U.S. P. 709846) describes an ammonia generator for laundry purposes.

Naef (Ger. P. 115249) evolves pure ammonia from ammonium chloride and magnesia in a continuously acting chamber.

The following patents also refer to this subject:—Henderson (B. P. 15836, of 1885); Brison (Ger. P. 34030); Pampe (described in Fehrmann's *Ammoniakwasser*, 1887, p. 67); Chevalet (B. P. 8819, of 1886); Holgate (B. P. 3384, of 1890); Whiteside (U.S. P. 534935); Bachmann and Sulzer (U.S. P. 573956); Stroh and Osins (U.S. P. 710221); Brunck (B. P. 8287, of 1903); Hirzel (Ger. Ps. 88953 and 91717); Francke (Ger. Ps. 165309 and 169444); Abendroth (U.S. Ps. 712891 and 792379); Adriaanse (Fr. P. 355971); Bossé (U.S. P. 1051383); Kresz (Ger. P. 226109); Brassert and Bacon (U.S. P. 1123232); Marr (B. P. 6291, of 1913; Fr. P. 470696); W. H. Wright (U.S. P. 1114843); Fabry (B. P. 337, of 1914).

Cf. also the apparatus described *infra* for sulphate of ammonia.

Absorption of the Ammonia Vapours in Water.

For the manufacture of liquor ammoniæ generally only *distilled water* can be employed which is obtained for chemically pure liquor by condensing steam from steam boilers in tin-lined cooling-worms; for "technically pure" liquor it is frequently obtained by the condensation of water from the steam used for the indirect heating of the apparatus. Ordinary water, which always contains more or less calcium salts, yields ammoniacal liquor, turbid by the secretion of extremely finely divided calcium carbonate; it also causes incrustations in the absorbing-apparatus which strongly interfere with the action of the cooling-apparatus, and may even cause obstructions. Condensed steam-water, on the other hand, may contain admixtures of oily matters from which it must, if necessary, be purified by a suitable filter. On the whole the preparation of "chemically pure liquor ammoniæ" differs from that of the "technically pure" article merely by the extent to which the purification of the gas has been carried; for the technically pure article, *e.g.*, the caustic-soda washers may be left out. Where water free from lime salts is at disposal, it may, of course, be employed for preparing technically pure liquor ammoniæ.

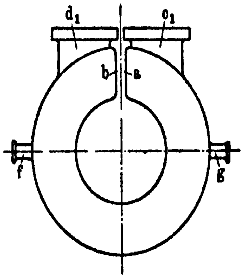
Absorbing-apparatus.—The absorption of ammonia by water produces a considerable amount of heat, and necessitates the *cooling* of the absorbing-vessels. These are frequently ordinary closed iron tanks, lined with lead, two or more combined to a set, and all of them provided with an inside coil of pipes for cooling-water. These tanks are used in turns; that which contains the strongest liquor receives the fresh ammonia gas as it comes from the purifiers, and its contents are run off, when they are saturated up to the desired point, whereupon the tank is filled with fresh water and now receives the stream of gases as the last of the set.

More efficient and usually preferred for continuous work are absorbing-vessels, shaped as *tubular coolers*, similar to those used for the pre-heating of the gas-liquor. In these the water to be saturated is *inside* the tubes, which causes a better subdivision of the stream of gas, and more efficient cooling by the water surrounding the tubes on the outside. The tubes are perpendicularly arranged, and at the top connected with a column, into which the water to be saturated enters continually at the top, and flows down from one basin to another. At the bottom the saturated liquor continuously runs out through a tube in which a hydrometer is floating, so that the working of the apparatus can be checked. All of this is like the Savalle column, described in Part II., pp. 927 *et seq.*

Of course the cooling must be particularly well effected, if the strongest liquor ammoniæ is to be made. At outside temperatures up to 15°, a maximum percentage of 37·4 per cent. NH_3 may be attained; at summer temperatures only 35·6 per cent. (=0·880 sp. gr.) can be reached. For this purpose the absorbing-vessels must be cooled down to 15° to 18°, or 18° to 20° respectively.

The absorbing-apparatus for continuous work, constructed by the Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft, has been shown *supra*, p. 1373, in connection with the other plant.

FIG. 283.



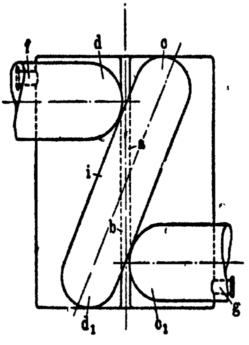


FIG. 284.

Only exceptionally, and exclusively for the preparation of chemically pure liquor ammoniæ, *stoneware receivers* are employed, similar to those used for the condensation of hydrochloric and nitric acid. A special kind of such receivers for the absorption of gases and vapours are those patented by Cellarius and Lehmann (Ger. P. 232864); they have the advantage of presenting to the gases twice the active surface possessed by the ordinary apparatus of the same kind. This is owing to their being constructed as a cylindrical ring, with a radial diaphragm separating the entrance and exit pipes for the gases, as visible in Figs. 283 and 284, showing a horizontal and a perpendicular section of the apparatus.

In the periodical style of making liquor ammoniæ, the absorbing-vessel receiving the fresh gas is emptied when its contents have got up to the strength required; the liquid contained in the last vessel is then run into it, and the last vessel is filled up with fresh water. In the continuous style of work there are as a rule only two absorbing-vessels, placed one above the other, communicating by an overflow-pipe from the top of the upper vessel going down to the bottom of the lower vessel. At first both of them are filled with water; when the contents of the first vessel have attained the proper strength, the supply of water to the top vessel is started, and is regulated so that the hydrometer in the outlet pipe always shows the proper strength.

In starting the work, when the fresh ammonia gas meets fresh water, the absorption of the gas is so violent that a vacuum is formed and the whole apparatus is shaken; but this does no harm in the case of iron vessels.

Sometimes the contents of the absorbing-vessels are not run straight into the carboys or tanks for carriage, but first into large-sized *collecting-vessels*, provided with a hand-worked stirring arrangement, which allows of regulating the strength with absolute equality.

Solid Ammonia.

This is the name given by the Chemische Fabrik Bettenhausen, Marquart & Schulz (Ger. P. 124976, of 1901), to a mixture of 3 to 5 parts sodium stearate, dissolved in 10 parts aqueous liquor ammoniæ, or else in 80 per cent. spirit of wine, made at 40° C. with 85 to 90 parts liquor ammoniæ of 25 to 33 per cent. NH_3. This mixture has a consistency nearly like that of solid paraffin; already on lying in the air, more quickly when gently heated, it gives up the whole of its NH_3, leaving only the sodium stearate behind.

Absorption of Ammonia by Hygroscopic Salts.

Ormandy, Walker, and Holroyd (B. P. 27985) absorb the ammonia by strong, or even supersaturated solutions of hygroscopic salts, preferably calcium chloride. The vessel containing the solution should be made to revolve, or be fitted with agitators.

Carriage and Storage of Liquor Ammoniæ.

The marketable liquor is usually run from the absorbers straight into the vessels for carrying it by rail, or otherwise. For chemically pure liquor these are *glass carboys*, for the technical liquor mostly cylindrical iron vessels, lined with lead both inside and outside; but glass carboys are employed also for the technical liquor, if the distance is not considerable or small quantities are concerned. The carboys should not be quite full, and must be kept in a cool place, lest they should be cracked by pressure of gas. They must be very tightly corked to prevent loss of ammonia by evaporation, which can be hardly altogether avoided when the liquor is kept in stock for some time. For large quantities *wrought-iron drums or tank-wagons* are used, which, however, give rise to red precipitates of iron oxides, and hence can only be employed for the crude article. The purer article is sent out in tinned iron drums. Sometimes "galvanized" iron drums are used; but it would seem that the zinc coating is gradually dissolved by the ammonia, especially if any air can enter.

Pennock and Morton (*J. Amer. Chem. Soc.*, 1902, p. 377; *Chem. Centr.*, 1902, i., 1180) have established the following facts concerning *the action of ammonia on iron.* If the iron be *completely* free from rust, concentrated ammonia not merely has no action on it, but even prevents the formation of rust, since this takes place only in the presence of *free* carbonic acid. When, however, concentrated ammonia is in contact with iron, partially covered with fresh rust, the rusting-process is promoted. If the iron be *completely* covered with a layer of rust, it is no more acted upon by concentrated ammonia.

The Board of Trade prescriptions for the carriage of liquor ammoniæ are quoted later on, p. 1406.

If the liquor is not at once sent out, but must be *kept in store* for some time, the filled carboys and iron drums must be placed in *cool localities.* The glass carboys are closed by good corks, enveloped in parchment paper, or by stoneware plugs, but both of these must receive a protective covering of plaster of Paris. The vessels, especially in the case of strong liquor, must not be exposed in the summer season to the direct heat of the sun; otherwise their contents may begin to boil, and not merely carboys, but even iron drums are cracked. For the same reason the vessels must never be filled up right to the top, so that the liquor may have room for expansion at higher temperatures.

Curphey (Chief Inspector of Alkali Works) strongly recommends protecting the liquor during storage against loss of ammonia by evaporation by a thin top-covering of oil (*Chem. Trade J.*, 1915, p. 496).

Uses of Liquor Ammoniæ.

These are extremely multifarious. Its most extensive employment is in the industries of dyeing, bleaching, scouring of wool, calico-printing, in the manufacture of colouring matters, the extraction of indigo, of cochineal, etc.; and in the preparation of a large number of chemical and pharmaceutical products. Considerable quantities are used in the industry of artificial silk (the ammoniacal cupric-oxide process). Benson and Crites use it for extracting resin from wood (*J. Ind. Eng. Chem.*, 1915, p. 918).

Testing of Liquor Ammoniæ.

Methods for a complete analysis of ammoniacal liquor have been given in Chapter XII., pp. 1277 *et seq.* In this place we mention only the commercial tests for the liquor ammoniæ of trade.

The percentage of ammonia in this liquor is nearly always ascertained by means of the hydrometer, for which the tables on p. 1297 may serve; but it must not be overlooked that these are valid only for the temperatures stated. In lieu of the figures for specific gravity, it is usual in Germany to employ the hydrometer of Baumé or Beck, in France that of Cartier; a table given in the Appendix will permit the reduction of these degrees to specific gravities.

Technically pure liquor ammoniæ should be colourless (even when exposed to the light for some time), clear, and not smelling too much of empyreuma. Sulphides ought to be entirely absent, as shown by lead-paper. Pure liquor ammoniæ for pharmaceutical purposes ought to be free from chlorides and cyanides (in which case, when it is neutralized by nitric acid, silver nitrate produces no opalescence), and should be almost free from empyreuma. The latter is especially perceptible on neutralizing the liquid.

Kupfferschläger (*Bull. Soc. Chim.*, xxiii., p. 256) prescribes proving the presence of *tarry matters* in liquor ammoniæ by the red colour which is produced by pouring a few drops of it into a test-tube containing a few cubic centimetres of colourless nitric acid diluted with a quarter of its volume of water. According to Wittstein (*Dingl. polyt. J.*, ccxiii., p. 512) the pink colour is not produced if the nitric acid be at once supersaturated with ammonia, but only on partial saturation, and it is destroyed by an excess of alkali. Both chemists ascribe it to the action of nitric acid on aniline, etc. Lehmann (Wagner's *Jahresber.*, 1864, p. 195) many years ago made a similar observation.

Tests for Pyridine.—H. Ost states (*Z. anal. Chem.*, xxiii., p. 59) that pyridine can be detected by its smell when nearly neutralizing the ammonia. By distilling the liquid, collecting the distillate in hydrochloric acid, evaporating and extracting the residue with absolute alcohol, a solution is obtained containing but little ammonium chloride. This is removed by addition of platinum chloride, and on evaporation of the alcoholic filtrate the platinum-pyridine double chloride separates in characteristic forms. The testing for pyridine by the smell can be conveniently carried out by soaking a piece of filtering paper with the liquor; after the ammonia has volatilized, the smell of the (less volatile) pyridine comes out more distinctly. That smell is still more perceptible, if a sample of the liquor is exactly neutralized with sulphuric acid; any excess of this should be taken away by adding a little ground chalk.

In order to test for pyridine, Künzel (*Fischer's Jahresber.*, 1890, p. 468) neutralizes 100 c.c. liquor ammoniæ with dilute sulphuric acid, with good cooling, adds a little caustic-soda solution, dilutes to 400 c.c., and distils off one-third during an hour. The distillate is mixed with 10 g. mercuric chloride, diluted to 400 c.c. and again distilled. The distillate ought not to require more than 2 c.c. decinormal soda (=0·00948 per cent. pyridine) before showing a neutral reaction against methyl orange.

Quantin (*Comptes rend.*, cxv., p. 561) performs the quantitative estimation of the pyridine bases in liquor ammoniæ by precipitating the ammonia as $Mg.NH_4.PO_4$, filtering, converting the organic bases contained in the filtrate into chloroplatinates, and separating those by means of absolute alcohol.

Pennock and Morton (*J. Amer. Chem. Soc.*, 1902, p. 377; *Chem. Centr.*, 1902, i., p. 1181) employ the following tests for commercial liquor ammoniæ:—(1) *Carbonic acid.*—Evaporate 100 c.c. of the liquor with 5 c.c. caustic-soda solution to about 20 c.c. To this residue add 50 c.c. water and a little phenolphthalein, cool down to 10° C., and exactly neutralize with sulphuric acid, avoiding any excess whatever of the acid. Then add 10 c.c. decinormal sulphuric acid, boil for two minutes, and after cooling titrate back with decinormal caustic-soda solution. (2) *Organic substances* (apart from pyridine).—Put 10 c.c. of the liquor into a 300 c.c. Erlenmeyer flask, add 20 c.c. 1/50 normal potassium pyrochromate and 50 c.c. dilute sulphuric acid (1 : 3); boil gently during twenty minutes, and, if necessary, fill up again to 50 c.c. After cooling, add an excess of 1/50 normal ammonio-ferrous sulphate and titrate back with 1/50 normal potassium permanganate, until a faint pink colour remains for some time. Add the cubic centimetres of $K_2Cr_2O_7$ and $KMnO_4$ used, and deduct the cubic centimetres of ammonio-ferrous sulphate; also the quantity of $K_2Cr_2O_7$ required in a blank test. The result is stated in cubic centimetres of 1/100 normal $K_2Cr_2O_7$ per 100 c.c. liquor ammoniæ. (3) *Pyridine.*—Neutralize 100 c.c. of the liquor, kept cold, almost completely with dilute sulphuric acid (1 : 5). Cool down to 20° C., add 1 or 2 drops of methyl-orange, and neutralize exactly with acid or alkali as may be required. Then distil the solution, and collect 70 c.c. of the distillate in a receiver containing 30 c.c. cold water. If the pyridine present does not exceed 2·5 g. per litre, the 100 c.c. present in the receiver contain all the pyridine. Cool down to 10°, add a little phenolphthalein and a solution of mercuric chloride till the colour has been discharged; then add another 4 drops of $HgCl_2$ solution. This precipitates any NH_3 still present. Phenolphthalein is reddened by NH_3, but not by pyridine. The filtrate is titrated with normal sulphuric acid and methyl-orange; 1 c.c. normal $H_2SO_4 = 0{\cdot}070$ g. pyridine. *Cf.* also the methods for estimating the pyridine in crude ammoniacal liquor, described *supra*, p. 1286.

Other *organic substances of a tarry nature* are proved, according to Bernbeck (*Pharm. Zeit.*, 1890, p. 694) by putting a layer of the liquor ammoniæ on to the top of crude, concentrated sulphuric acid; if such tarry substances are present, a red ring is formed at the zone of contact.

Pfeiffer (Lunge and Berl's *Chem. Techn. Unt. Meth.*, 6th ed., iii., p. 367) has found many relations between the percentage of empyreumatic substances and the smell of liquor ammoniæ. He recommends to test for the former in the constant checking of the work by the following short method. To 10 c.c. of the sample add 30 c.c. dilute sulphuric acid (1 : 5) and 10 or 20 c.c.

centi-normal permanganate solution, heat to gentle boiling for five minutes, decolorize by 10 c.c. centi-normal oxalic acid, and retitrate with 1/100 normal permanganate until a faint pink colour appears. The total amount of permanganate used, less the 10 c.c. of oxalic acid, is an expression of the organic substance contained in the liquor. Pfeiffer found in various samples of commercial liquor ammoniæ a consumption of between 0·5 and 22 c.c. permanganate.

According to Krauch (*Prüfung der chemischen Reagentien auf Reinheit*, 2nd edition, p. 164) commercial "chemically pure" liquor ammoniæ must stand the following tests: (1) *Pyridine and Chlorides.*—Ten c.c., diluted with 30 c.c. water, should remain colourless after supersaturating with nitric acid, and this liquid should not show any change on the addition of silver nitrate. (2) *Volatility.*—Fifteen g. liquor, on being evaporated in a porcelain capsule on the water-bath, should leave at most slight traces of a residue. (3) *Metals.*—Five c.c., on addition of 20 c.c. water and a few drops of ammonium sulphide, should show no change. (4) *Sulphuric Acid.*—Ten c.c., after being supersaturated with acetic acid, should give no reaction with barium chloride even after prolonged standing. (5) *Carbonic Acid.*—Ten c.c., on being mixed with 10 c.c. water and 40 c.c. lime-water, should show no turbidity.

Klotz (*Chem. Zeit.*, 1911, p. 141) describes an apparatus for testing liquor ammoniæ which contains no new features.

III. MANUFACTURE OF ANHYDROUS LIQUID AMMONIA.

The possibility of converting gaseous ammonia by pressure and cold into the liquid state has been known for a long time past. Already in 1799 von Marum asserted that he had liquefied the gas by a pressure of 3 atm., and later on Fourcroy and Vauquelin, and Guyton de Morveau were believed to have done so by cooling down to −40° to −43°·5; but probably the gas employed for their experiments was not absolutely dry.

In 1823, Faraday published in *Phil. Trans.*, cxiii., pp. 189 *et seq.*, the work done by him, at the suggestion of Davy, on the liquefaction of gases. He describes there an experiment, shown up to this day in lectures on chemistry, which consists in heating argentic chloride, saturated with dry ammonia gas, in one of the limbs of a closed two-limb glass tube, the empty limb of which is cooled by ice; the ammonia volatilized is here condensed to a colourless liquid. A year later Busey made the all-important observation that by the volatilization of liquefied sulphur dioxide at ordinary pressure a lowering of the temperature down to $-57°$, at diminished pressure down to $-65°$ can be attained; from this dates the industry of ice and cold-producing machinery. In 1845 Faraday succeeded by means of Thilorier's cold-producing mixture (solid carbon dioxide and ether) to convert liquid ammonia into a solid, crystalline mass, fusing at $-81°$.

Up to that time the liquefied gases, of which, apart from ammonia, carbon dioxide (Natterer, 1844), sulphur dioxide (Davy, 1823), chlorine (Faraday, 1823) and several others had been prepared, possessed hardly any but scientific interest; but Busey's observation led to the invention of machines for producing ice on a technical scale, the first of which was that constructed by Carré. Through the enormous development of the industry of ice and cold, liquefied ammonia has become a very important article of trade as the generally preferred means of producing cold. Apart from its consumption for this purpose, the great advantages in the cost of transit possessed by liquid ammonia in comparison with ammoniacal liquor containing at most 35 per cent. NH_3, and the possibility of preparing from it such liquor of any desired strength without requiring special apparatus for that purpose, have imparted to liquid ammonia a constantly increasing application in chemical industry, so that its manufacture is nowadays probably the most remunerative branch of the industry of ammonia generally.

We refer in this connection to several special treatises on that subject, viz., Teichmann, *Komprimierte und verflüssigte Gase*, Halle, 1908; Hardin, *Liquéfaction des gaz*; German edition, by I. Traube, Stuttgart, 1900; Bronn, *Verflüssigtes Ammoniak als Lösungsmittel*, Berlin, 1905; Bamberger, *Über die Industrie komprimierter und verflüssigter Gase*, Wien, 1909; Urban, *Laboratoriumsbuch für die Industrie der komprimierten und verflüssigten Gase.*

General Principles.—Up to the moment of liquefaction, the apparatus for manufacturing anhydrous liquid ammonia from raw gas-liquor is exactly the same as that described *supra* for the production of chemically pure liquor ammoniæ. From this reason, the liquefaction of ammonia is as a rule only carried on in connection with that of liquor ammoniæ, which has the advantage that, according to the more or less favourable market for one or the other of these products, either of them can be manufactured at will. It should be noticed that, according to practical experience, the producing-capacity of the ammonia stills in the case of using them for the manufacture of liquid ammonia is essentially increased through the aspirating action of the gas-compressor.

The manufacture of liquid ammonia is carried out by the simultaneous application of cooling and compressing, the cooling being principally applied for taking up and carrying away the heat, set free by the compression of the gas. At 0° the ammonia is liquefied by a pressure of 4·19 atm.; at +15° it requires 7·14 atm. (*Chem. Ind.*, 1901, p. 99). The apparatus employed is practically identical with that used for liquefying carbon dioxide or sulphur dioxide.

Purification of the Gaseous Ammonia before Compression. Removing the Moisture.—The primary condition for manufacturing a satisfactory description of liquid ammonia is, of course, the application of *dry* and specially *purified* ammonia gas. From this reason it was formerly usual to prepare liquid ammonia not directly from crude gas-liquor, but from most highly concentrated liquor ammoniæ, sometimes even from such obtained by saturation under pressure, from which the gaseous ammonia was aspirated by the compressor, and submitted to drying before compression to the liquid state. For this purpose, very high columns were employed, into which the liquor ammoniæ was introduced about half-way up, the upper, well-cooled part of the column serving for absorbing the ammonia liberated below at a somewhat higher pressure than in the ordinary distilling-process, so that a supersaturated solution was formed which, on relieving the pressure, gave up part of the ammonia without application of heat, and nearly in the dry state, owing to the considerable lowering of the temperature produced by this action, which reduced the tension of the aqueous vapour to a minimum. The last traces of moisture were taken away from the gas by passing it through towers filled with caustic lime and caustic soda.

R. Pictet (*Zsch. für kompr. und verflüss. Gase*, 1897, p. 46) recommended, as the best way for removing the aqueous vapour from ammonia gas, its circulation in a very efficient refrigerator, on whose walls the aqueous vapour is precipitated in the shape of hoar-frost, aided by strong pressure, which, however, must not go up to the liquefying of the ammonia. The gas coming out from here is practically anhydrous ammonia. By repeating this compression and expansion, apart from the moisture also organic bases and other impurities are secreted in a liquid form. According to the investigations of Strombeck (*Proc. Franklin Inst.*, vi., p. 92; *Fischer's Jahresber.*, 1892, p. 324), the commercial anhydrous liquid ammonia, found in the trade at that time, on evaporation left a yellow liquid of penetrating smell, and frequently needle-shaped crystals of ammonium sesquicarbonate. That yellow liquid contained several alcohols, from methylated spirits upwards, acetone, lubricating oil, etc.; these admixtures seem to be the cause of the explosions sometimes occurring in ammonia-ice machines. He therefore proposed in his U.S. P. 477089, of 1892, to purify ammonia before compression by passing it at 90° C. over fused sodium, which retains all the above impurities, with evolution of hydrogen. The latter is removed by means of palladium sponge, which absorbs 800 times its volume of hydrogen, and of which 250 g. suffice even for a large plant. Only then the gas is passed into the condenser, and furnishes a liquid of 99·995 per cent. NH_3.

Bertelsmann (*Lehrb. d. Leuchtgasind.*, i., p. 519) purifies the ammonia gas by drying it over caustic lime and passing it into a gas-holder, the bell of which is luted by oil, which retains ethyl alcohol, benzol, pyridine, and other organic substances. The condensation and evaporation is repeated several times, until there is no more residual matter present, and only then the liquid ammonia is put into the vessels for transporting it. This process of purifying the ammonia gas, after intense drying, by means of oil, is also prescribed by the "Bamag" Company.

Testing the Ammonia Gas for Moisture.—Even by the best drying apparatus, it is hardly possible to remove the moisture from ammonia gas below 0·5 per cent., this remainder being removed later on during the compression of the gas, as described *supra*. It is decidedly necessary to convince oneself whether the drying has been carried to the requisite extent, by testing a sample of the gas. The ordinary methods for carrying out tests for moisture by means of caustic lime, potash or soda, soda-lime, etc., are not sufficiently reliable for the purpose. Pure, concentrated sulphuric acid answers the purpose, if employed in the way employed by Köhler during a number of years for the daily testing, which combines accuracy, simplicity, and speed of execution (Lunge and Köhler's *Industrie des Steinkohlenteers*, 1912, ii., p. 308). It is founded on the increase of weight of the acid. Ninety-eight g. pure H_2SO_4 absorb 34 g. pure NH_3. If, therefore, gaseous ammonia is passed into 9·8 g. sulphuric acid with the proper precautions and in a suitable apparatus, until the exact point of neutrality, the increase of weight must not exceed 3·4 g. Any excess of weight over this amount is caused, in the absence of organic substances, by the moisture contained in those 3·4 g. (=4·5 litres gaseous NH_3) of ammonia. Köhler employs for this test the apparatus shown in Fig. 285. It consists of a flask, A, holding about 75 c.c., with a ground-in hollow glass stopper, into which are sealed the enlarged gas-entrance tube B, and the calcium-chloride tube C, the outlet tubes of which are provided with a loop of platinum wire, by which the apparatus can be suspended in a balance. There must be two such apparatus, as every test has to be made in duplicate, and these must be regulated for passing through the same amount of gas. This is approximately attained by making the inlet tubes from the same glass tube, which is drawn out before the blow-pipe into a capillary, and cutting the latter in the middle by a stroke of the file. These inlet tubes are by means of india-rubber tubing joined to the lower end of the inlet tubes B, in such a way that they dip equally far into the sulphuric acid, tinged by methyl orange. Each apparatus is charged with 50 c.c. dilute sulphuric acid, corresponding to exactly 9·8 g. H_2SO_4; when filled, it weighs from 75 to 80 g.

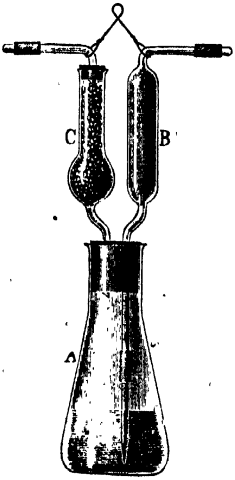


FIG. 285.

The apparatus, exactly weighed, are placed before and during use in dishes, filled with bits of ice. They are joined to the ammonia main by a T-piece with glass taps, by which the current of gas is regulated in such a way that the saturation takes about fifteen to twenty minutes. Before starting the test, the gas stagnant in the connecting-tube (which enters into the producing-pipe) escapes. In order to prevent any absorption of moisture from the air, the calcium-chloride tubes of the apparatus are connected with a small stationary drying-tower. Small gas bubbles are noticed to ascend only in the beginning (until the air has been driven out of the inlet tubes) and at the end of the test (when the sulphuric acid is nearly saturated). At the moment when the colour of the liquid changes (which takes place almost instantaneously on the saturation of the acid by NH_3), the glass taps are closed, the apparatus are taken out of the ice, well dried on the outside, and allowed to stand before weighing until they have assumed the temperature of the outside air. During this time the liquid rises up in the entrance tube, owing to the ammonia still contained in it, and completely fills up the widened part of B. Since the air, standing in the absorbing vessels above the liquid, does not contain a trace of ammonia, the apparatus can be weighed directly, without replacing that air by dry air from without; for the same reason the drying tubes C may be filled with the more active granular calcium chloride.

The difference of weight before and after the absorption is composed of the following items:—(1) The weight of the NH_3, taken up by the sulphuric acid, which is known to be = 3·4 g; (2) the weight of any ammonia taken up by the ammonium sulphate solution in A, which is determined by titrating in the same flask with decinormal acid; (3) the weight of the water contained in the absorbed ammonia. By adding the weights *sub* (1) and (2), and deducting the sum from the difference of weight of the apparatus before and after the absorption, we learn the percentage of water originally contained in the whole of the ammonia absorbed.

Intermediate Vessels for the Gaseous Ammonia.—The compressing-pump generally does not take the ammonia gas straight from the pipe conduit coming out of the drying- and purifying-apparatus, but as a rule from an interposed gas-holder, luted with heavy mineral oil, holding from 5 to 10 cbm., and serving as regulator for the pressure. Where a certain production of liquor ammoniæ is carried on at the same time, such an intermediate vessel is most useful, because it allows of making more gas than the compressor can take, passing this excess of gas into the absorbing-vessels for liquor ammoniæ.

Where, as described *supra*, the ammonia gas is got from most highly saturated liquor ammonia, such a gas-holder is not required as regulator; but where raw ammoniacal liquor is worked directly for liquid ammonia, it does very good service.

According to the Julius Pintsch Aktien-Gesellschaft these intermediate vessels, if they are not made of very large dimensions, may have disagreeable effects. For this reason, and on account of the considerable expense, that firm makes the compressors take the gas straight away, without an intermediate gas-holder, and avoids the risk of excessive changes of pressure by interposing one or more closed vessels and a pressure indicator.

Compressors for liquefying Ammonia Gas.—This work is done precisely in the same way as for liquefying other gases, and indeed for so many other purposes where highly compressed air or other gases are required. In all cases the heat produced by the compressing machinery must be carried away; this is partly done by cooling devices connected with that machinery, partly by subsequent cooling. As in all other cases, the compressors may be of the single-acting or of the double-acting type; and they may effect the work all at once, or in several stages. For the liquefaction of ammonia only single-acting or at most two-stage compressors are used, just as for carbon dioxide or sulphur dioxide. The necessary valves are always spindles, pressed by spiral springs against the valve seat. All the parts coming into contact with ammonia must not be made of a metal acted upon by ammonia, like yellow or red brass, bronze, copper, etc., but must be made of steel. Both the aspirating- and forcing-valves must be placed within the body of the compressor, not in the aspirating- and forcing-pipes, and they must be so arranged that they can be at any time revised or renewed, without having to remove any piping.

Of course both the pistons and piston-rods must be constantly and thoroughly oiled to prevent excessive wear and tear, as well as a loss of power by friction. Some of this oil is carried away with the compressed gas by volatilization or in a mechanical way, and must be removed from the gas by a proper oil-separator between the compressor and the condenser, of which there are various types. The De la Vergue Refrigerating Machine Co. at New York employs for their standard compressors a special oiling apparatus, together with an oil-separator behind the pump.

Ammonia compressors are built both of the upright and of the horizontal type. The latter is more usual in Europe, the former is almost universally employed in America. They are built both with direct action, or for being worked with pulleys and belts. The latter style of compressors is sometimes preferred on the ground that they are less liable to accidents in cases of excessive pressure; but they consume more fuel than those working with direct action, and these are just as safe to work, if in the high-pressure conduit a safety-valve is interposed, such as are supplied for this purpose by the Maschinenfabrik Sürth at Sürth, near Cologne (*Chem. Ind.*, 1905, p. 429).

The same firm supplies two-stage compressors for ammonia gas which are preferred to the one-stage pumps by large factories, as they do more work, and that more quickly, and are not subject to as much wear and tear as the one-stage compressors. They are also preferred where, owing to an insufficient quantity of cooling-water, the work must be done at a higher pressure than 8 to 10 atmospheres.

Cooling of the Compressed Gas (Intermediate Coolers and Condensers).—The critical temperature of compressed ammonia gas is higher than the temperature of ordinary cooling-water. Hence it is possible to liquefy the gas by appropriate cooling with water.

In the case of working with two-stage (or higher-stage) compressors the heat produced at every phase of the compressing process is taken away by *intermediate coolers.* Since these have not at the same time to fulfil the task of removing the *latent* heat, set free in the liquefaction, they need not have very large dimensions, and can be mostly placed within the body of the compressor in the shape of pipes surrounded by flowing water. For liquefying the gas, after it has reached its final pressure, serve the *condensers*, placed immediately behind the compressor, and consisting either of one or more coils of pipes placed in a cooling-vat, or by a set of pipes, over which water is constantly flowing. Such coolers are, *e.g.*, provided in the ammonia-compressing plant of the Maschinenfabrik Sürth, on the principle of the counter-current. The type of coolers recently employed by that firm requires only a fifth to an eighth of the cooling-surface required by the older systems.

H. C. Gardner (U.S. P. 1129477) describes a cooling-apparatus for condensing ammonia from the gaseous to the liquid stage.

The coils of the condensers, as well as their connections with the compressor, are made of seamless iron pipes; the valves and other moulded pieces are made of cast steel. As packing for the flanges, lead or rubber rings are employed, the faces of the flanges being provided with grooves for receiving these rings.

Where the liquid ammonia is run from the condensers straight into the vessels for carrying it away, a *collector* should be interposed between the condenser and the running-off apparatus, which in the course of work is partly filled with liquid, partly with gas, admitting to take off the liquid from time to time without interfering with the condenser. This arrangement has also the advantage that any unliquefied gases, like air, etc., can be let out at the highest point of the apparatus.

Combination of Apparatus for the Manufacture of Liquid Ammonia.

Many such combinations have been made, but all of them on the same principle, identical with that used for liquefying other gases. We therefore show only two such combinations, one for working on a comparatively small scale, and another for large production, and refer for the rest to C. Schmitz, *Zeitschrift für die gesamte Kälteindustrie*, 1895, pp. 161 and 225; and Bertelsmann, *Lehrb. d. Leuchtgasindustrie*, i., p. 519.

The apparatus shown in Figs. 286 to 288, for the production of liquid ammonia, on a moderate scale, is supplied by the Germania Engineering Works, formerly I. Schwalbe & Son, of Chemnitz. It consists of an ammonia compressor with steel valves, placed on a box which in its upper portion holds the condensing-worm, and in its lower portion a welded wrought-iron cylinder in which the liquid ammonia from the worm is collected. The cooling-water enters at the bottom and issues at the top. The gaseous ammonia aspirated by the compressor is liquefied in the worm by means of combined cooling and pressure, and runs into the cylinder, from which it is forced

FIG. 238.

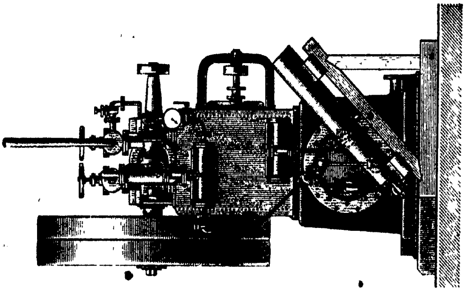
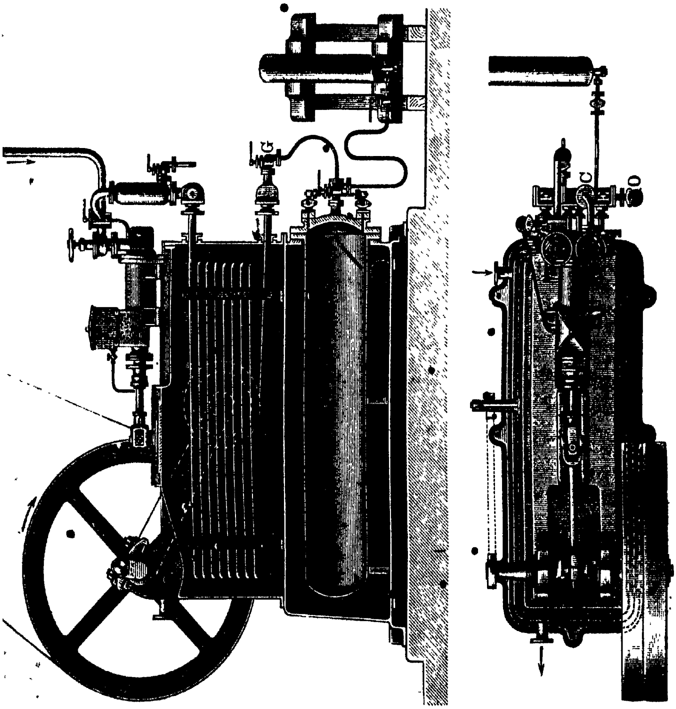


FIG. 237.



by a pipe, reaching to its bottom, into steel bottles, like those employed for liquid carbon dioxide, holding about 20 kg.

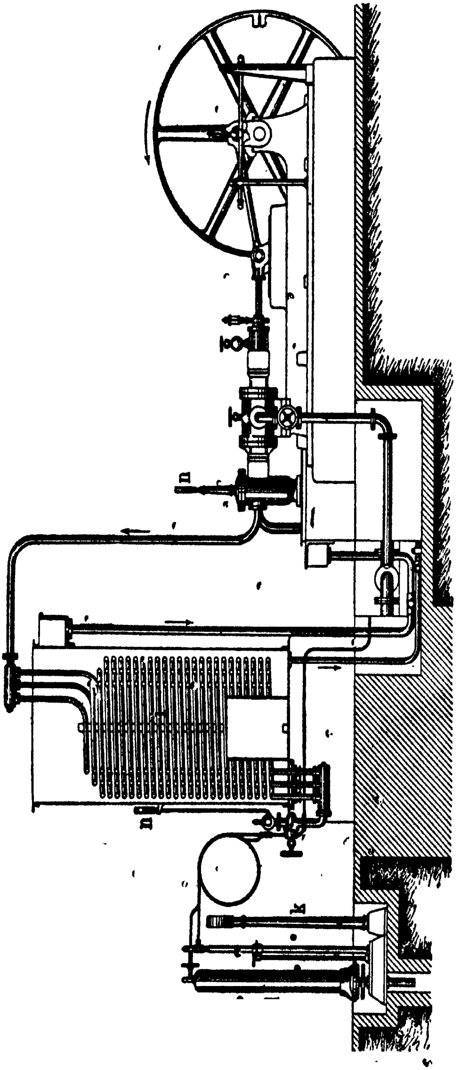


FIG. 289.

Figs. 289 and 290 show an ammonia compressor for a duty of 80 kg. per hour, as built by the Maschinenfabrik Sürth.

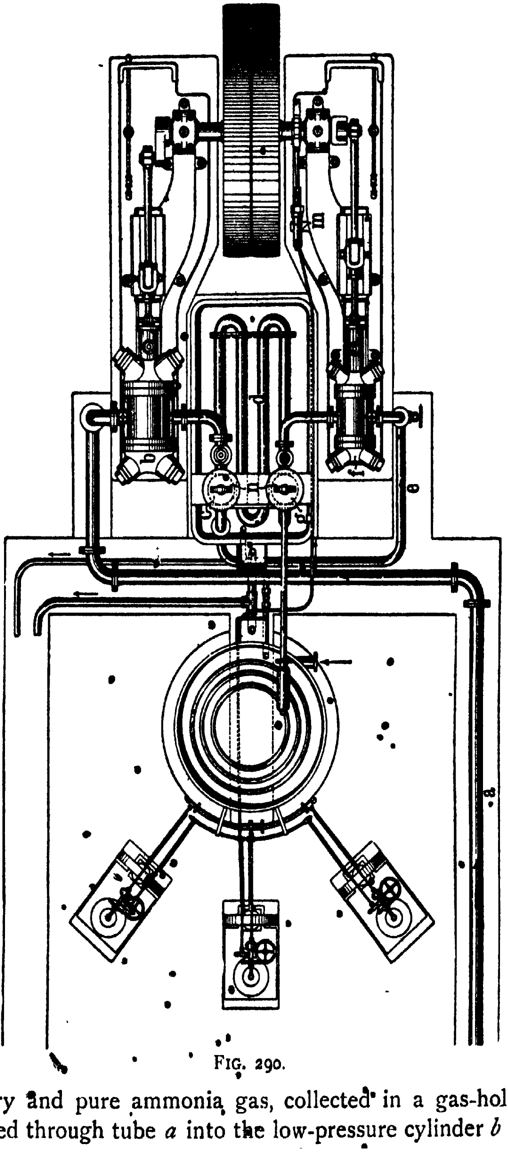


FIG. 290.

The dry and pure ammonia gas, collected in a gas-holder, is aspirated through tube *a* into the low-pressure cylinder *b* of the two-stage compressor, where it is compressed to about 3 atmospheres. After passing through the oil-separator *c*, the hot gas gets into the intermediate cooler *d*, where it is cooled down to the temperature of the flowing water, and is then aspirated through pipe *e* into the high-pressure cylinder *f*, where it is brought to the liquefying-pressure of 8 to 10 atmospheres; any oil carried away from this press is retained in the oil-separator *g*. Compressor *f* possesses two suction- and two pressure-valves, attached to both sides of the cylinder, with common suction- and pressure-pipes. The pumps are driven by a common crank-shaft, set in motion by a pulley and belt. After leaving the high-pressure cylinder *f*, the gas is compressed to such an extent that it is liquefied at about 8 atmospheres' pressure by the subsequent cooling in one of the apparatus, mentioned *supra*, p. 1395. The condenser *i*, shown in the diagram, consists of a triple coil of seamless pipe, without any socket connections, with common collecting-pieces at the entrance and the exit ends; the cooling-water flows from below into the cooling-jacket surrounding the coils, into which the gas to be liquefied enters from the top. The liquid ammonia collects in the lower part of the coils, and runs into the transportation-cylinders *l*, standing on the carriages *k*, which admit of reading off the weight of the cylinders *l* at any time. The air is got out of the bottles *l*, and thus an article as free as possible from air is obtained by means of a vacuum pump *m*, which forces the air through water in order to retain any ammonia. On the two oil-separators *c* and *g*, there are pressure-gauges *n* with safety-valves.

The Badische Anilin- und Sodafabrik now manufactures liquid ammonia from the ammonia produced by the process of Haber and Rossignol, *supra*, p. 1074. They *purify* it from dissolved gases (uncombined nitrogen and hydrogen), by fractional distillation, preferably under pressure (B. P. 25259, of 1912; Fr. P. 458950; Ger. P. 277526).

Fig. 291 (from Teichmann, *Komprimierte und verflüssigte Gase*, 1908, p. 90) shows a plant for the production of liquid ammonia on a large scale, with application of P. Mallet's revolving column (which we describe later on in connection with the manufacture of ammonium sulphate). This combination is especially interesting, because it allows of producing at the same

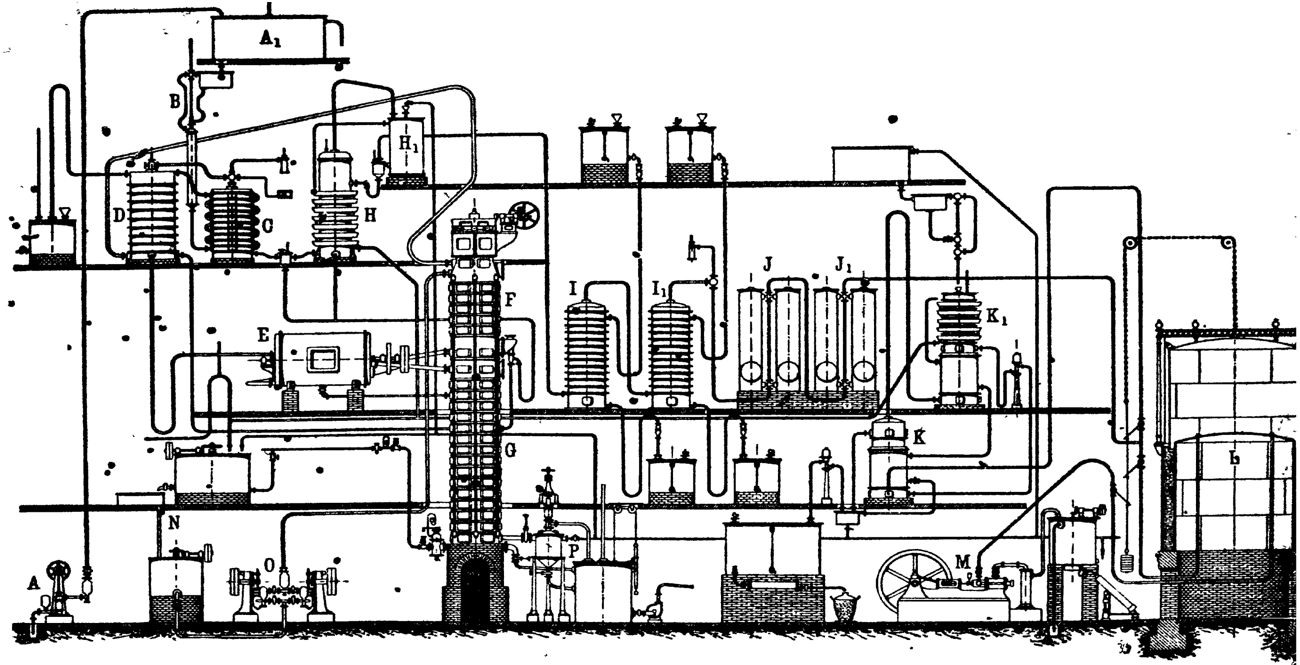


FIG. 291.

time *concentrated solutions of ammonia* in a column, provided with mechanical agitating-gear, without being troubled by the secretion of crusts of lime. A is the pump, A_1 the storing-tank for gas-liquor which runs through the measuring-device, B, into the preheater, C, and from this into the decomposer, D, where it is heated by the vapours escaping from the column F to such an extent that a great portion of the carbon dioxide and hydrogen sulphide, combined in the raw liquor with ammonia, are set free and escape, whilst the ammonia remains behind, dissolved in the gas-liquor. CO_2 and H_2S are retained in the horizontal milk-of-lime washer E, and at the same the fixed ammonia is driven out by the lime. Milk-of-lime of the constant concentration of 15° Bé. is prepared in the two superposed agitating-vessels N. Pump O conveys the milk-of-lime into the upper part of the column F, in which the vapours coming from the lower part, G, are also purified from CO_2 and H_2S, so that only hot ammonia gas, saturated with aqueous vapour, escapes at the top of F into the decomposer, D, where it is cooled by the crude gas liquor meeting it in the opposite direction; whilst the milk-of-lime flows from F into the mixer E, where it gets mixed with ammonia water coming from D.

The mixture, now converted into a paste by the precipitated calcium carbonate, flows through the distilling-column G, where it is completely boiled out by steam, rising up in the column, the fixed ammonium salts being decomposed, and the ammonia set free being driven out. That ammonia, together with steam, rises up in the column, and the boiled-out water runs out continuously at the bottom of G, the outflow being regulated by the float P. In the coolers H and H_1 the ammonia-gas is cooled by fresh water, the condensate flowing back into the column. After being thus freed as much as possible from steam, the ammonia gas next passes through the purifying-column I, where it meets a solution of caustic soda, and I_1 where it meets oil, and then through the cylinders J and J_1, which are charged with caustic soda, burnt lime, and charcoal. Being thus purified from CO_2, H_2S, moisture, and empyreumatic matter, the gas is now either conducted into the absorbers K and K_1 for the manufacture of liquor ammoniæ, or into the gas-holder L, from which the compresser M aspirates the gas and compresses it, whereupon it is liquefied in the condenser attached to M.

Various Processes for making Liquid Ammonia.

Krebs (B. P. 17313, of 1897) gradually evolves NH_3 from liquor ammoniæ by heating, returns the vapour through the solution under treatment, separates the aqueous vapour by cooling, and compresses the pure NH_3 with further application of cooling.

Morris (U.S. P. 712704) describes a condenser for liquefying ammonia gas.

Frerichs (U.S. P. 586950) purifies liquid ammonia by redistillation. According to his U.S. P. 905415, he heats commercial ammonium sulphate to about 200° C., in order to volatilize any carbon compounds, blowing in air at the same time. He then raises the temperature first to 350°, then to 400°, in order to produce the reaction: $(NH_4)_2SO_4 = NH_4HSO_4 + NH_3$. The free NH_3 is collected and condensed; the ammonium pyrosulphate, formed from the acid sulphate when heating to 400°, is dissolved in water and employed for absorbing impure NH_3.

Pollard (B. P. 6274, of 1914) manufactures liquid anhydrous ammonia without mechanical compression, by placing the ammonia gas in contact with nitrate of ammonia in a dry crystalline state, whereby the ammonia is liquefied in large quantities, forming a solution with the salt. On application of heat to this solution, the ammonia gas is freely given off again, and can be condensed into the liquid state, leaving behind the dry salt, ready to liquefy another quantity of gas. All the gas is evolved at a temperature of 88°. A number of other salts of ammonium, sodium, and potassium act in the same way as the ammonium nitrate.

Hirth (U.S. P. 1100015) describes a cooling-apparatus, consisting of a condenser, a receiver for the liquid ammonia, a receiver for the waste gas placed above the condenser, and a connecting-piece between the waste-gas receiver and the receiver for liquid ammonia.

Muir (*J. Gas Lighting*, 1915, cxxix., p. 756) describes a plant for manufacturing liquid ammonia at a cost of $3203·07 per 179 tons, as compared with $3596·57 per 179 tons of sulphate of ammonia, 24·5 per cent. It is convenient to prepare liquid ammonia only when and where there is a market for it.

Storage and Carriage of Liquid Ammonia.

Liquid ammonia is stored in the well-known steel-bottles, *i.e.*, cylindrical vessels (bottles, drums) made of seamless "Mannesmann tubes," with a valve attached to them. Such a bottle is shown in Fig. 293, on a scale of 1 : 15, and the valve in Fig. 292, on a larger scale, as supplied by the Maschinenfabrik Sürth.

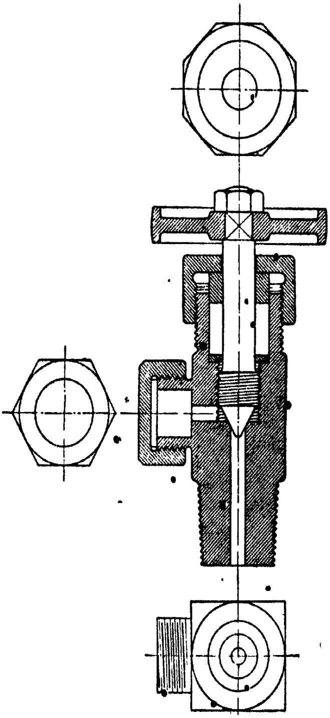


FIG. 292.

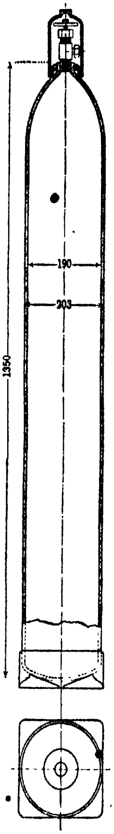


FIG. 293.

The following table shows the normal conditions for

Mannesmann bottles, intended for keeping and carrying liquid ammonia, for holding 10, 20, or 45 kg.

Capacity in kg. liquid ammonia.	10.		20.		45.	
a in case of rolled tubes. *b* in case of cold-drawn tubes.	*a*	*b*	*a*	*b*	*a*	*b*
Contents, litres	18·6	18·6	37·2	37·2	84·37	84·37
Outside diameter, millimetres .	159-205	203	205	203	205	203
Thickness of plate, „ .	45-5·25	4·5	5·25	4·5	5·25	4·5
Length without valve, „ .	1190-780	780	1420	1420	3010	3010
Empty weight, without valve, but inclusive of protecting cap and foot, kg.	25·27	24	44	38	87	73

For *carriage* the lighter bottles are preferred as they are anyhow safe enough, on account of the lower cost of transit, since the weight of the empty bottle far exceeds that of its contents. For temporary *storage* larger cylindrical vessels of corresponding strength may be used without hesitation, but such are not admitted for railway transportation in Germany, although for liquid sulphur dioxide, carbon dioxide, and chlorine such tank-wagons are allowed.

The following rules have been laid down for the transportation of liquid ammonia by the German Railway Companies: "Liquid ammonia must be sent out in vessels made of wrought-iron, ingot-iron, or cast steel. These vessels must be officially attested to stand an internal pressure of 30 atmospheres, without showing any permanent deformation or leakiness; and this test must be repeated once every three years. They must not *in maximo* contain more than 1 kg. ammonia for each 1·86 litres cubic capacity. They must in a conspicuous place show the official statement of the weight of the vessel in the empty state, inclusive of valve and protecting cap, of the contents allowed, and the date of the last pressure-test."

According to experiments made by A. Lange, the danger of explosion is not materially increased by the air generally contained in liquid ammonia. When heating the steel bottles, the pressure increases gradually, until the vessel is quite full; if the heating is continued, the pressure increases at first rapidly, afterwards again slowly. If filled according to the German railway rules, the bottles can be heated to 65° C. without any fear; only two-thirds of the tested pressure is then attained, and the bottles never give way unless heated above 68° C.

The manufacture and testing of the vessels intended for liquid ammonia is described *in extenso* by Frerichs, in *J. Ind. Eng. Chem.*, 1912, pp. 80-88, with many illustrations.

Safety valves are not attached to drums for transportation, but only to stationary store-tanks for liquid ammonia. Such valves are made, *e.g.*, by the Maschinenfabrik Sürth.

For *the carriage of liquid ammonia as a cargo on board ship*, the English Board of Trade has issued regulations, according to which it must be packed in iron vessels, tested to a pressure of 675 lb. per square inch, and stored in a part of the ship beyond the influence of any heat from boilers or furnaces, and remote from the living quarters. The *aqueous solution of ammonia*, of sp. gr. 0·880, should be conveyed in drums of about 12 gall. capacity, with an empty space equal to 5·33 per cent. left in each drum. The drums should be capable of withstanding a pressure of 66 lb. per square inch, and should be packed in cases with no more than four drums in a case, the interstices being filled with sawdust; but for short voyages, as to Ireland or the Continent, no cases are required. The drums should not be exposed to the heat of the sun or of a fire, and should not be covered with a black tarpaulin. Ammonia solution of sp. gr. 0·959 and upwards is exempted from these prescriptions.

The *filling of the drums* is carried out either straight from the condensing-worm, or from a store-tank by means of a pipe with several branch-tubes, to which the drums, which stand on an automatic valve, are attached by spring-steel pipes. The bottles must not be filled quite up; a gas-space of 12½ per cent. of the total contents must be left empty.

The drums are closed by a screw valve, as shown in Fig. 292, p. 1404, made of steel, provided with a lateral branch for the gas, and a screw-connection for discharging, and protected by a screwed-down cap. A valve distinguished by small weight, together with complete reliability, is the "arborventil" of the Aktien-Gesellschaft für Kohlensäure-

Industrie at Berlin, shown in Figs. 294 and 295, in natural size. Its weight is only about 0·700 kg., against 1·3 kg. of other constructions. The body of this valve consists of

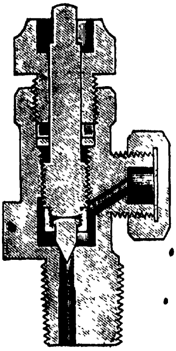


FIG. 294.

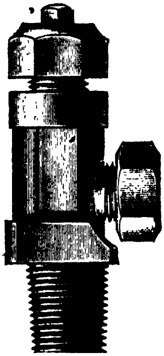


FIG. 295.

wrought-iron, the spindles, etc., of hardened cast-steel, with asbestos packings.

The use of liquid ammonia in laboratories and factories

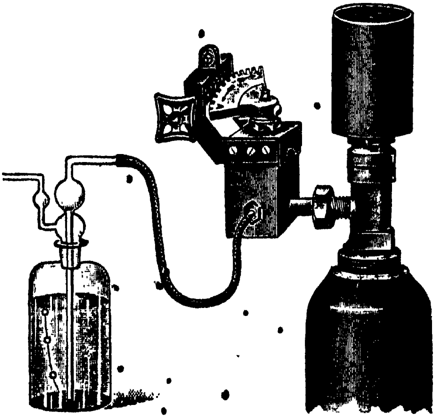


FIG. 296.

is essentially promoted by such suitable discharging-valves. Another construction of these, viz., throttle-valve of the Aktien-Gesellschaft für Kohlensäure-Industrie at Berlin is shown in Fig. 296. This throttle-valve serves for regulating the outflow of gaseous ammonia from the drums; it consists of a spindle, with a toothed segment, movable by means of a volute-wheel in such a way that a slight turning of the hand-wheel causes only a hardly perceptible opening of the valve, and therefore only a correspondingly slight change in the quantity of the gas issuing. This throttle-valve is screwed on to the emptying-neck of the valve by means of a nut. For taking out some gas, first the drum-valve is opened, and then the current of gas is regulated by turning the hand-wheel on the throttle-valve.

Properties of Commercial Liquid Ammonia.

Commercial liquid ammonia is a colourless, easily mobile liquid, containing up to 99·9 per cent. of NH_3. The impurities found in it are: water, pyridine bases, hydrocarbons of the benzol series, and lubricating oil, which remain on evaporating the ammonia as a strongly-smelling liquid of brownish-yellow colour. Sometimes inorganic solid substances are present, such as ferric oxide, which comes from the rusty parts of the machinery.

Strombeck (*Proc. Franklin Inst.*, vi., p. 92) found in six samples of American liquid ammonia from 96·984 to 99·180 per cent. NH_3, 0·010 to 0·079 water, 0·117 to 1·644 "colourless liquid," 0·004 to 0·087 ammonium carbonate, 0·004 to 0·035 lubricating oil, and up to 0·007 per cent. sand, oxide of iron, etc. In the "colourless liquid" he found acetone, methyl-alcohol, ethyl-alcohol, and isopropyl-alcohol. Lange and Hertz (*Z. angew. Chem.*, 1897, p. 224) found in 20 kg. of liquid ammonia a residue of 187 c.c., consisting of water, pyridines, acetonitrile, ethyl-alcohol, ammonium carbonate, benzene, and naphthalene, a little lubricating oil and solid substances (ferric oxide).

Complaints have been made by the consumers of liquid ammonia in the cold-producing industries that these impurities cause both a diminished production of cold and an attack on the metal of the compressors. According to Lange (*Woch. f. Brau.*, xv., p. 93), sometimes these impurities cumulate in the machinery, and then produce a sensible damage to it.

Applications of Liquid Ammonia.

The principal application of liquid ammonia is in the *cold-producing industries;* but also in the *chemical industries*, especially that of aniline colours, it is more and more used in lieu of ammoniacal liquor (spirit of hartshorn), and this is likely to extend more and more, since it is produced at a comparatively low expense. Liquid ammonia not merely saves the cost of transit for the large amount of water contained in liquor ammoniæ, but has over this the great advantage that the ammonia contained in it can be used at will in the shape of gas, or in that of an aqueous solution; and, moreover, that its storage requires much less room, and no fragile vessels, as carboys, etc.

Liquid ammonia is much employed as a *solvent* for chemical purposes. *E.g.*, Craig (Ger. P. 92172) utilizes the fact that it easily dissolves ammonium nitrate for separating this salt from potassium sulphate in the decomposition of potassium or sodium nitrate with ammonium sulphate.

Wilton (Ger. P. 113201) employs it for the *purification of crude anthracene*, as the impurities are easily soluble in liquid ammonia, whilst anthracene itself is not so. He also (Ger. P. 113675) employs it for *separating potassium from sodium cyanide*, the latter salt being much more soluble in it than the former.

Divers (*Proc. Roy. Soc.*, xxi., p. 109) observed that by passing dry ammonia over ammonium nitrate a liquid containing 50 per cent. free ammonia is produced, which may lead to a further utilization of liquid ammonia.

Considerable quantities of liquid ammonia are now used for preparing *cyanides*. By the action of dry gaseous ammonia on fused sodium the highly reactive sodium amide, $NaNH_2$, is formed, which Pfleger (Ger. P. 126241 of the Deutsche Gold- und Silberscheide-Austalt) converts almost quantitatively into sodium cyanide by fusion with coal, eventually with the intermediate formation of disodiumcyanamide. The same amide, according to Pfleger, can be employed as condensing agent, in the place of caustic alkalies, for transforming phenylglycocoll into indoxyl, with much higher yield, and it therefore plays an important part in the manufacture of *artificial indigo.*

Liquid ammonia has been proposed for inflating air-ships to be gasified there, in lieu of hydrogen; but A. Sander (*Chem. Zeit.*, 1915, p. 325) considers that there are various objections to this proceeding. The lifting power of NH_3 is only 0·52 kg. per cubic metre, compared with 1·20 kg. for hydrogen, and volume for volume it is ten times as costly as hydrogen. It has also a destructive action on the material of the envelope, and an unpleasant effect on the occupants of the air-ship in case of leakage; moreover, mixtures of ammonia and air between the limits of 16·5 and 26·8 per cent. NH_3 by volume are dangerously explosive.

Up to the present there are no statistics on the extent of the production and sales of liquid ammonia.

Analysis of Liquid Ammonia.

The methods for this purpose are enumerated by Urban in his *Laboratoriumsbuch für die Industrie der verflüssigten und komprimierten Gase*, pp. 1 *et seq.*

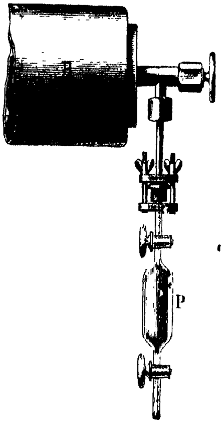


FIG. 297.

The *direct estimation of the ammonia* offers great difficulties. As a rule only the impurities are estimated, and the remainder is assumed to be pure ammonia.

The *practical valuation* of liquid ammonia is confined to the estimation of the residue left on evaporation, without inquiring into its composition. Bunte and Eitner (*J. Gasbeleucht.*, 1897, p. 174) allow the liquid by its own pressure to enter from the steel bottle B into a pipette P (Fig. 297), and weigh the residue left on slow evaporation, after having at last heated the pipette to 70° or 80° in a current of dry air, with several caustic-potash bulbs attached. This process, as Lange and Heffter have shown (*Chem. Ind.*, 1898, p. 2), and Urban has confirmed, is inaccurate, since benzene, acetonitrile, alcohol, and even pyridines are carried away by the air at the ordinary temperature.

Urban (*Chem. Zeit.*, 1897, p. 720) employs a pipette (Fig.

298), holding about 70 c.c., 30 mm. wide, contracted below into a 5 mm. tube, 5 or 6 cm. long, divided into $\frac{1}{20}$ c.c., whilst the remainder is divided into whole cubic centimetres. This facilitates the measuring of the ammonia and of the residue; the specific gravity of the former may be taken =0·617, that of the residue = 0·8, in the case of much water = 0·9.

The Linde Ice-machine Company (*Z. angew. Chem.*, 1897, p. 224) employ a glass tube, 27 mm. wide, with handle, contracted below into a tube 9 mm. wide. It holds 30 c.c. up to the place where a little hole is made in the wider tube; the narrow tube contains 3 c.c. divided into 10 parts. The apparatus is filled from the iron bottle until the liquid runs out of the side hole; it is then allowed to evaporate, and the residue read off in per cent.

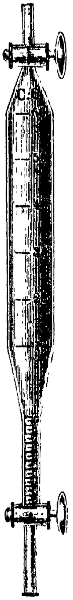


FIG. 298.

Lange and Hertz (*Z. angew. Chem.*, 1897, p. 224) object to this that the specific gravities of the liquid ammonia and the residue are not the same, and that some of the latter may be mechanically carried away by quick evaporation, whilst on slow evaporation water may be condensed inside. They therefore employ a special tube, taking account of the different specific gravities (0·68 at −38° C. for NH_3, 0·9 as the average of the residue). The upper part holds, up to the point 49 c.c. 33·3 g. NH_3; the narrow lower part 1·1, divided into 15 parts, each of them = 0·2 per cent. The whole is left for spontaneous evaporation, a nickel stopper being put in the top of the instrument. The contents of the tube boil regularly, and after three hours all is finished, or in half an hour, if the narrow part is placed in water.—An error in this method is caused by the quantity of ammonia left in the residue (up to 25 per cent.); but there is a simple way out of all the difficulties, and for ordinary purposes the just-described method (which is much handier than any working with glass-tap pipettes, and which is probably used more than any other by those who have to deal with liquid ammonia) is sufficient. The manufacturers ought to guarantee a maximum of 1 per cent. residue to be found by this method.

An apparatus for testing liquefied ammonia has been constructed by F. W. Frerichs, at St Louis (*Amer. Inst. Min. Eng.*, 28th December 1908; *J. Ind. Eng. Chem.*, 1909, pp. 362 *et seq.*). He criticizes the methods used up to that time, which are founded on the fact that the impurities present in liquid ammonia have higher boiling-points than this compound. In America ammonia is considered to be pure enough for the manufacture of ice, if a sample of 4 oz. does not leave a visible residue on evaporation. The attraction of moisture from the air during the sampling must be avoided as much as possible; the sample is placed in a glass flask about 5 in. high, which is at once closed by a cork through which passes a glass tube, open at both ends and turned sideways below, and is left to evaporate. But this test is inaccurate, because the impurities partly go away along with the ammonia.

W. D. Richardson (*J. Ind. Eng. Chem.*, ii., p. 96) reports on the work done by him with the method of Frerichs. He examined also the uncondensed gases, contained in the drums above the liquid ammonia, and found in these enormous differences, from 0·6 to 330 c.c. per gram of ammonia, which is lost on blowing these gases off. According to him, normal liquid ammonia should not contain upwards of 0·1 c.c. total residue per 100 c.c. of ammonia; the uncondensed gases, dissolved by the liquid ammonia, should not amount to more than 0·6 c.c. per gram of ammonia, and the drum should not show any perceptible loss of weight after blowing off the uncondensed gases.

The analysis of anhydrous ammonia is also treated by Lucion and Paepe (*Bull. Soc. Chim. Belg.*, 1906, p. 347; *Z. angew. Chem.*, 1908, p. 497). Commercial anhydrous ammonia contains rarely as much as 99·9 per cent. NH_3, sometimes down to 97 per cent. The impurities are: methylic, ethylic, and isopropylic alcohol, acetone, acetonitrile, amines, pyridines, benzene, naphthalene, sometimes ammonium carbonate, a little lubricating oil, ferric oxide, sand, etc. The authors employ for its analysis a modification of Bunte and Eitner's method (*vide supra*, p. 1410). One hundred and sixty to 170 g. of the liquid ammonia is placed in a Kroecker bomb, and the gas issuing from this is very slowly passed through three large U-tubes, containing caustic soda, into a measured quantity of seminormal sulphuric acid, contained in two bottles of 3·5 litres' capacity, placed in succession and connected in such manner that the acid cannot get back. In the end dry air, free from CO_2, is passed through the apparatus; and the bomb is heated on a water-bath for half an hour. The carbon dioxide present is estimated in another sample by absorption in aqueous NaOH solution.

CHAPTER XIV

THE COMPOSITION AND ANALYSIS OF AMMONIACAL LIQUOR, AND PROPERTIES OF ITS CONSTITUENTS

WE have seen in the preceding chapter that, by subjecting gases containing ammonia to a combination of cooling and washing processes, we obtain an aqueous solution of ammonium salts which we call "ammoniacal liquor." We do not in this place include liquors which are obtained by the direct action of sulphuric, sulphurous, or hydrochloric acid on such gases, but only those obtained by the action of water alone. The most important source of ammoniacal liquor is the purifying process to which ordinary coal-gas must be submitted, and hence such liquor is commonly called "gas-liquor." The solutions obtained from coke-oven or blast-furnace gases are equally derived from coal, and are quite similar in character to gas-liquor, and they are treated in exactly the same way, so that we shall in the future always include them when considering the former. This would also be the case with liquors obtained from gas-producers, if that method became a working process. Even the liquors obtained from fermented urine, or by the destructive distillation of bones and other animal refuse (pp. 1154 and 1162), although not identical in composition with those derived from the treatment of coal, are so similar that the same principles are followed in working them up into commercial articles.

Composition of Ammoniacal Liquor.

Ordinary gas-liquor contains the following substances:—

a. *Volatile at Ordinary Temperatures.*

Ammonium carbonates (mono-, sesqui-, bi-).
Ammonium sulphide, $(NH_4)_2S$.

Ammonium hydrosulphide, $NH_4.HS$
Ammonium cyanide.
Ammonium acetate (?).
Free ammonia.[1]

b. *Fixed at Ordinary Temperatures.*

Ammonium sulphate.
Ammonium sulphite.
Ammonium thiosulphate (hyposulphite).
Ammonium thiocarbonate.
Ammonium chloride.
Ammonium sulphocyanide (thiocyanate).
Ammonium ferrocyanide.

Also the salts of organic bases, especially those of the pyridine series; phenols, naphthalene, and other matters of a tarry or "empyreumatic" character.

The more important of these substances will be described towards the end of this chapter. The term "fixed" in this case is not to be understood in its absolute sense, but in so far as the compounds of ammonia with carbonic and sulphhydric acids can be removed from their solutions by simply exposing them to a sufficiently prolonged boiling, certainly not in the state of unchanged vapours of ammonium salts, but dissociated into less complicated compounds; but the ammoniacal salts, called "fixed," are not removed from their solutions by boiling, or are only very partially decomposed by most prolonged heating of the solutions, so that the ammonia contained in them must be recovered by heating the solutions with caustic lime, which sets the ammonia free. This is an important distinction in the practical working-up of gas-liquor.

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[1] The presence of free ammonia in gas-liquor is doubted by many chemists, but is asserted by two competent observers, Gerlach and Tieftrunck (Wagner's *Jahresber.*, 1877, p. 1065). It must certainly be formed by hydrolytic action from ammonium salts. G. M. Gill (*J. Gas Lighting*, 1911, cxiv., p. 362) found in the gas-liquor from the collecting-tank of an English gas-works 7·4 grains, from the hydraulic main 73·0 grains free ammonia per gallon. *Cf.* also the analyses of Wanklyn, Mayer and Hempel, and Grossmann, quoted *infra.*

The proportion of the total ammonia to the "fixed" ammonia varies according to circumstances. Fixed ammonia naturally occurs in much larger proportion in the hydraulic main, where the first condensation takes place, than in the condensers and scrubbers; it may amount to more than 50 per cent. of the total ammonia in the former, against 1 or 2 per cent. in the latter. This proportion is, moreover, influenced by the composition of the coal. *E.g.*, the percentage of ammonium chloride in the gas-liquor will naturally depend upon the percentage of chlorine in the coal distilled. The percentage of fixed ammonia will also be influenced by the temperature of the gas-retorts, by the temperature to which the gas-liquor has been exposed, by its exposure to the air (which oxidizes the sulphide into thiosulphate and perhaps higher than that), and by the general methods of washing and scrubbing the gas (J. H. Cox, *J. Gas Lighting*, etc., Report of the Leeds Meeting, 6th Oct. 1883).

Concerning the *influence exerted by the style of the retorts for gas-making on the composition of the gas-liquor*, experiments made by Carpenter have had the following results:—

	Ferrocyanides, calculated as HCN, grams *per* litre.	Chloride, calculated as Cl, grams *per* litre.	Ammonia, grams *per* l.			Grams *per* litre.		
			Total.	Easily decomposable salts.	Not easily decomposable salts.	CO_2.	H_2S.	HCN.
Horizontal retorts .	0·17	3·13	34·68	2·21	32·47	40·37	3·84	0·43
Slanting retorts .	trace	5·25	25·54	5·23	20·31	36·96	1·95	0·17
Perpendicular retorts	trace	6·11	17·60	4·32	13·28	13·86	4·06	0·50

Bertelsmann (*Lehrb. de Leuchtgasind*, i., p. 468) points out that no definite conclusions can be drawn from these figures, as there is no indication how far the results may have been influenced by the other conditions of working.

Undoubtedly the composition of the gas-liquor is greatly influenced by the fact whether *the hydrogen cyanide has been washed out of the gas or not*, since this operation leads to the absorption of some ammonia and hydrogen sulphide (*cf. e.g.* Bueb's Ger. P. 112459). On this point Linder has made experiments, with the following results:—

The gas-liquor contained grams *per* litre.	Without washing out the cyanide.	When washing out the cyanide.
Ammonium ferrocyanide	0·12	1·01
Chlorides, calculated as HCl	7·76	3·26
Carbon dioxide	25·71	20·57
Hydrogen sulphide	6·61	2·68
Hydrogen cyanide	0·68	0·03
Ammonia, total	27·52	19·15
„ easily decomposable salts	21·76	14·68
„ not easily decomposable salts	5·76	4·47
Sulphur as sulphide	72·80	38·50
„ as sulphate	0·70	26·90
„ as sulphocyanide	23·40	22·40
„ as sulphite and thiosulphate	3·10	12·20

In the process of washing out the cyanide, part of the ammonia remains in the "cyanogen mud" in the shape of soluble and insoluble ferrocyanammonium compounds and as sulphate, and part of the hydrogen sulphide in the shape of ferrous sulphide; when working up this mud for ferrocyanide, that part of the ammonia is recovered as sulphate or caustic ammonia.

The *oxidizing action of the air* is also of great influence on the gas-liquor. If air is mixed with the gas before washing out the ammonia, the percentage of not easily decomposable salts in the gas-liquor is increased by the oxidation of the sulphur compounds. The same action takes place, if the gas-liquor is kept in stock for some time, as proved by Linder's analysis of the same liquor before and after storage:—

In 1 litre there was contained:	Immediately after obtaining the liquor.	After six months' storage.
Ammonia, total	27·52 grams	29·80 grams
„ as easily decomposable salts	21·76 „	19·20 „
„ as not easily decomposable salts	5·76 „	10·60 „
Sulphur, total	8·55 „	9·12 „
„ as sulphate	0·70 per cent.	4·50 per cent.
„ as sulphocyanide	23·40 „	57·90 „
„ as thiosulphate	3·10 „	16·40 „
Carbon dioxide	25·51 „	21·22 „
Hydrogen sulphide	6·61 „	2·05 „
Hydrogen cyanide	0·68 „	0·00 „
Ferrocyanide, calculated as HCN	0·068 „	0·00 „

Since by the increase of the not easily decomposable salts the expense of working up the gas-liquor is increased by the greater consumption of lime, it is advisable not to keep the liquor longer than necessary in stock.

This has been especially insisted upon by J. H. Cox (*J. Gas Lighting*, 6th October 1883). The following tables, *showing the composition of gas-liquor* (pp. 1261, 1262), have been constructed by myself from the materials supplied in the paper by Mr Cox; but the thiosulphate is not, as there, included in the "volatile" salts, since experiments made by myself have convinced me that it decomposes on boiling hardly more than the chloride.

According to Wanklyn (*Gas-Engineers' Chemical Manual*), virgin gas-liquor from the first parts of the plant may contain free ammonia, because this is more quickly absorbed than the other constituents, but in passing through the scrubbers enough CO_2 is absorbed to convert all the free ammonia into carbonate. If the same liquor is used over and over again for scrubbing, a good deal of the ammonium sulphide is also converted into carbonate, H_2S being given off.

Detailed analyses of gas-liquor, obtained under different conditions, are given by L. T. Wright (*J. Soc. Chem. Ind.*, 1886, p. 655).

According to information received by me from one of the largest German ammonia-works, it is calculated there that liquor from English coals contains from 15 to 20 per cent. of the total ammonia in the "fixed" state, that from Westphalian coals 5 to 10 per cent.; while in liquor from Saxon coal the fixed ammonia may amount to two or three times as much as the volatile.

We will still refer to some recent analyses (by Mr Linder) contained in the *Forty-second Report on Alkali, etc., Works*, for the year 1905, pp. 35, 36. Many other analyses of ammoniacal liquors are given in previous alkali reports, and in the *Forty-fourth Report*, pp. 53 *et seq.*, where especially the proportion of ammonium chloride to fixed ammonia and the cyanogen compounds are dealt with.

I. *Table showing the Properties and Composition of eight samples of Gas-liquor obtained from the same Coal, but taken from different points in the Condensing- and Scrubbing-plant.*

	Condensed in the hydraulic main.	Another point of the hydraulic main	Liquor from first condenser column.	From second condenser column.	From third condenser column.	From fourth condenser column.	From first washer.	From finishing washer.
Colour	Very dull orange, turned black in air	Ditto.	Colourless	Almost colourless	Brown-red from light tar-oils.	Dark brown, from tar-oils	Colourless	Colourless
Specific gravity in deg. Twaddell at 15° C.	2¼	2½	7	15	23	24	4½	2
Ounces by distillation test	6·1	6·0	16·2	36·1	53·0	58·0	16·5	8·3
Ounces by saturation test	2·7	2·8	15·9	35·7	52·5	57·4	16·1	8·1
Am. sulphide, grains per gal.	364	440	2430	5000	7905 NH_3	8440	1592	1220
$= NH_3$,,	182	220	1215	2500		4220	796	610
Am. carbonate ,,	564	510	3384	8120		12126	4512	1690
$= NH_3$,,	200	81	1200	2880		4300	1600	600
Am. thiosulphate ,,	122	82	Trace	125	352	765	230	135
$= NH_3$,,	28	19	Trace	41	81	176	51	31
Am. sulphate ,,	8	34	...	...	...	...	...	...
$= NH_3$,,	2	9	...	...	...	...	...	...
Am. sulphocyanide ,,	112	130	91	Trace	...	...	112	27
$= NH_3$,,	25	29	2	Trace	...	...	25	6
Am. chloride ,,	1552	1455	119	155	201	107	88	38
$= NH_3$,,	493	462	38	50	64	34	28	12
Am. ferrocyanide ,,	...	Trace	22	41	125	375	...	...
$= NH_3$,,	...	...	5	10	30	90	...	...
Total ammonia, grains per gal.	930	920	2460	5480	8080	8820	2500	1260
Percentage of fixed ammonia in the total ammonia	59 p.c.	56 p.c.	1·8 p.c.	[illegible]·85 p.c.	2·2 p.c.	3·4 p.c.	4·2 p.c.	4·0 p.c.
Ammonia expressed as cwt. of sulphate per 1000 gallons	4·5	4·5	11·9	26·6	39·3	42·8	11·8	6·1
Value of liquor for sulphate-making.	Very small	Very small	Very good	Very good	Excellent	Excellent	Very good	Not quite strong enough

II. *Table showing the Properties and Composition of various samples of Liquor from different Coals, and from different points in the Condensing- and Scrubbing-plant.*

	Condensed liquor, passed through scrubber.	Another sample taken at different time.	Same liquor, exposed to air, high temperature.	Hydraulic main liquor.	Part condensed liquor, part hydraulic main.	From "Standard" washer before purifiers.
Colour	Yellow	Yellow	Bright orange	Dull yellow	Yellow	Colourless
Spec. grav. = deg. Tw. at 15°·5	4·5	4	3·5	2	3	4·5
Ounces by distillation test	10·00	8·25	6·90	5·60	6·60	10·00
Ounces by saturation test	8·30	7·00	4·25	3·40	4·90	10·00
Am. sulphide, grains per gallon	960	1216	630	576	220	1180
= NH_3 ,,	480	608	315	288	110	590
Am. carbonate ,,	2030	1156	800	...	1692	2540
= NH_3 ,,	720	410	283·5	193	600	900
Am. thiosulphate ,,	195	182	236	...	174	Trace
= NH_3 ,,	45	42	52·5	35	40	...
Am. sulphate ,,	...	Trace	39	...	9	...
= NH_3 ,,	...	...	10·5	6	2·5	...
Am. sulphocyanide ,,	338	243	472	...	90	...
= NH_3 ,,	75	54	105	36	20	...
Am. chloride ,,	567	403	891	...	693	32
= NH_3 ,,	180	128	283·5	301	220	10·1
Am. ferrocyanide ,,	Trace	...	...	...	31	...
= NH_3 ,,	...	...	...	...	7·5	...
Total ammonia	1500	1250	1050	860	1000	1500
Percentage of fixed ammonia	20	18·3	43	44	29	0·7
Ammonia expressed as cwt. sulphate per 1000 gallons	7·5	6·00	5·00	4·10	4·85	7·30
Value of liquor for sulphate-making.	Not good	Poor	Very poor	Not worth working	...	Very good

From the same report (pp. 46, 47) we take the following tables:—

Distribution of Sulphur in Ammoniacal Liquors from Various Sources.

Liquor (Average).	Per cent. Sulphur to Ammonia.	Sulphur. Per cent. of total.				
		Oxidation Products.				Sulphide.
		Sulphate.	Thio-cyanate.	Thio-sulphate.	Total.	
Coke-ovens (9 samples) .	27·9	3·2	6·7	6·7	16·6	83·4
Gas-works (6 samples) .	30·4	6·5	29·6	10·0	46·1	53·9
Shale-works (1 sample) .	9·7	4·5	Nil	43·2	47·7	52·3
Iron-works (1 sample) .	2·3	48·9	32·0	19·1	100·0	Nil

Distribution of Cyanogen in Ammoniacal Liquors from Various Sources.

Liquor (Average).	Per cent. cyanogen to ammonia.	Cyanogen. Per cent. of total.			
		Reaction products.			Hydrocyanic acid.
		Thio-cyanate.	Ferro-cyanide.	Total.	
Coke-ovens :—					
(1) Virgin (6 samples) . .	3·4	12	3	15	85
(2) Store tanks (11 samples) .	6·1	25	Nil	25	75
Gas-works (9 samples) . . .	8·9	68	7	75	25
Iron-works :—					
(1) Cooler (1 sample) . .	0·8	17	Nil	17	83
(2) Washer (1 sample) . .	0·6	100	Nil	100	Nil
Shale (2) samples	Nil	...	...	...	...

Ammonium Salts in Recovered Sulphur from Claus-kilns (Gas-works and Coke-oven Liquors).

Sample.	Moisture per cent.	Per 100 parts (undried) calculated as		Hydrocyanic acid in liquor. Grms. HCy per 100 c.c.
		NH_3.	$(NH_4)_2SO_4$.	
FROM GAS-WORKS LIQUOR. *Works* 1.				
First section:— Lumps, dry, crystalline; slightly discoloured. No smell	0·5	0·58	2·25	...
Second section:— Flowers and crystalline lump mixed; moist, discoloured. Smells of SO_2 . . .	6·7	1·72	6·67	...
Third section:— Flowers; wet, pale yellow. Smells of mirbane and SO_2	42·6	0·20	0·78	...
FROM COKE-OVEN LIQUOR. *Works* 2.				
Hot end:— Lumps, crystalline; discoloured and dark in colour .	...	0·54	2·09	0·039
Cold end:— Flowers; dull yellow, moist .	...	0·27	8·81	...

Further analyses of ammoniacal liquors from various sources are given in the *Report*, No. 43, pp. 33 *et seq.*, but the above-quoted analyses will be sufficient for our purposes.

A table showing the variations of the constituents of gas-liquor which occur on keeping it during some time, whereby the sulphide passes over into sulphate, thiosulphate, and sulphocyanate, is given by Linder in *J. Gas Lighting*, 1906, p. 642 (*J. Gasbeleucht.*, 1907, p. 1105).

The following analyses of gas-liquor, made by the most improved methods, are given by Mayer and Hempel in *J. Gasbeleucht.*, 1908, pp. 428 *et seq.* They show that the differences between two samples of the mixed liquor, taken in winter and summer, are not very serious, but all the more so those between two samples taken at the same time, one from the hydraulic main and the other from the well containing the mixed liquor. The volatile compounds in the former are only one-fifth of those in the latter, owing to the high temperature (nearly 100° C.) ruling in the hydraulic main, which causes a considerable dissociation of the volatile compounds. The "fixed" ammonia comes out very similarly in both samples, but that is only apparently the case, the liquor in the hydraulic main being much more concentrated than the mixed liquor in the well. The figures mean grams per litre.

	Well. Jan. 27, 1907.	Well. May 11, 1907.	Hydraulic main. May 11, 1907.
Total ammonia	18·600	17·152	5·794
Ammonia, volatile . . .	15·320	14·064	2·916
" fixed	3·284	3·088	2·880
Ammonium carbonate . .	40·834	35·260	4·751
" sulphide . . .	2·803	2·760	0·730
" thiosulphate . .	...	1·227	1·427
" sulphite . . .	...	trace	0·000
" sulphate . . .	0·295	0·228	0·229
" chloride . . .	7·404	7·380	7·216
" sulphocyanide .	...	1·820	1·000
" ferrocyanide . .	..	0·883	0·119
" cyanide . . .	...	0·0328	0·035

The following table gives a computation of the amounts of ammonia for the samples taken on 11th May 1907, at the same time from the well and from the hydraulic main. The figures signify grams NH_3 per litre, present in the shape of the salts enumerated :—

	Well.	Hydraulic main.
Total NH_3 found by direct distillation . .	17·152	5·794
" as calculated from the sum of the component salts	17·050	4·751
NH_3 present as carbonate	12·5000	1·6850
" " sulphide	1·3796	0·3650
" " thiosulphate	0·2820	0·0981
" " sulphate	0·0588	0·0590
" " chloride	2·3500	2·2971
" " sulphocyanide	0·4072	0·2240
" " ferrocyanide	0·0224	0·0080
" " cyanide	0·0464	0·0136

Hence the liquor in the well contains but a very small quantity of free ammonia (0·102 g.), but that in the hydraulic main the considerable amount of 1·043 g. per litre, owing to a far-going dissociation of the carbonate and sulphide. This free ammonia makes the liquor from the hydraulic main especially fit for the wet purifying process.

VALUATION OF AMMONIACAL LIQUOR.

This is frequently done at the gas- and tar-works by means of the *hydrometer*, for the sake of convenience. But this process is most deceptive; for the ammonium salts raise the density of the solution in an unequal degree, and free ammonia lowers it. The following table by Seidel (Hofmann's *Bericht über die Wiener Ausstellung*, i., p. 194) proves how unequal are the percentages of ammonia in different gas-liquors of the same specific gravity (at 15°):—

Degrees Baumé . .	2°.	2°·5.	3°.	3°·5.	4°.	4°·5.	5°.	6°.
Specific gravity. .	1·0138	1·0163	1·0208	1·0249	1·0280	1·0316	1·0352	1·0426
Per cent. NH_3 . .	1·16	1·30						
	1·42	1·43						
	1·50	1·63	1·63					
	1·77	1·77	1·76					
		1·98	1·90	1·87				
		2·18	2·10	2·00				
		2·65	2·38	2·24				
			2·45	2·40	2·55			
				2·72	2·72	2·79		
					2·90	2·85		
					3·40	3·06		
						3·40		
						3·53	3·67	3·74

Similar observations have been made by T. H. Davis (*Chem. News*, xxxviii., p. 193), and the tables on pp. 1261 and 1262, by Mr Cox, completely bear out the same conclusion. Fischer (*J. Gasbeleucht.*, 1909, p. 278) also proves by the examination of 28 samples of gas-liquor that there is no connection between its specific gravity and its percentage of ammonia.

It is therefore indispensable to ascertain the ammonia contents of gas-liquor by *chemical* methods. If in one and the same works, gasifying the same raw material, frequent tests have shown an almost equal composition of the gas-liquor at certain hydrometer degrees, the hydrometer may be used as a check, not leaving out of sight that the formation of ammonia is sensibly influenced by slight changes in the humidity of the air, the temperature of gasifying, etc.

The analytical methods employed for gas-liquor comprise in all cases the estimation of the total ammonia and that of the volatile ammonia, the proportion of fixed ammonia being found by deducting the volatile from the total ammonia; a complete analysis is only made exceptionally. For judging of the value of a liquor, the estimation of the total ammonia is most important; for the object of working it up, the estimation of the fixed ammonia and that of CO_2 and H_2S is necessary, because on this depends the amount of lime to be added in distillation, and to a certain extent also the dimensions of the distilling-plant. These must in all cases be ample, in order to make sure of regular work. In the modern style of apparatus, where CO_2 and H_2S are removed by dissociation, the addition of lime can be confined to that required for decomposing the fixed ammonium salts.

1. *Estimation of the Volatile Ammonia.*

Frequently only the volatile ammonium salts are estimated, the ammonia of which is given off on distillation without lime, and is indicated by direct titration of the liquor with sulphuric acid, without heating. The ammonium salts with stronger acids, *i.e.*, the sulphate, chloride, and sulphocyanide, were formerly left out of account, as the ammonia thus present hardly ever amounts to more than 0·3 per cent.

The usual way is, to employ the ordinary standard acid, which contains 0·04904 g. SO_4H_2 per cubic centimetre, and indicates 0·01703 g. NH_3. When litmus is employed as indicator, a certain volume of gas-liquor, say 20 c.c., should be first supersaturated with standard acid (for which purpose 40 c.c. will suffice in most cases), and boiled to expel all carbon dioxide and hydrogen sulphide; then the litmus solution is added and the excess of acid retitrated by standard alkali (soda or seminormal ammonia). In *direct titration* with acid a solution of litmus cannot be very well employed, because it is discoloured by sulphuretted hydrogen; in this case litmus-paper can be employed, which, after a little practice, does not take much time; or else some of the azo-colours are employed, which permit exact working in the cold and are not affected either by CO_2 or H_2S, of which the best known is the "methyl-orange." It is the dimethylanilineazobenzenesulphonate of soda, and it is not to be confounded with the "tropæolines," which yield much less precise results.[1]

In England it is usual to state the percentage of gas-liquor in "ounces." This refers to the number of ounces of real sulphuric acid (H_2SO_4) required for saturation by each gallon of gas-liquor, and the test is made as follows:—A standard liquid is prepared by diluting 16½ oz. of real sulphuric monohydrate, H_2SO_4, with water to the volume of a gallon. The specific gravity of the dilute acid ought to be = 1·068, according to the usual statement. This prescription, however, is useless without, at the same time, stating the temperature. At 15° C. an acid containing in 100 parts by volume 10 parts by weight of real H_2SO_4 will have the specific gravity 1·064; it is, of course, much better not to rely upon a specific-gravity test, but to test your standard acid in the usual way, say, with pure sodium carbonate.[2]

The test itself is performed by measuring off 16 liquid ounces of the gas-liquor to be examined, and running in the test-acid from a measure or burette graduated to liquid ounces, till litmus-paper indicates neutrality. The number of the measures of acid indicates the number of ounces of real sulphuric acid required for each gallon of gas-liquor. It is generally supposed that each degree Twaddell corresponds as nearly as possible to 8 oz. of sulphuric acid; *e.g.*, gas-liquor of 4° Tw. will saturate 8 oz. of acid. This, however, is anything but correct, as is best shown by Cox's tables, pp. 1261 and 1262. It is therefore altogether misleading and objectionable, as used to be formerly done, to double the figure found by Twaddell's hydrometer, and call this the "ounces" per gallon. This is generally to the advantage of the buyer, for nearly in all cases the Twaddell degrees × 2 indicate far below the actual value of the liquor in ounces.

The test as just described is called the "*saturation test*";

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[1] Compare the author's special directions in the *Technical Chemists' Handbook*, 1910, p. 242.

[2] This operation is described in every text-book of Analytical Chemistry; also in full detail in Lunge's *Technical Chemists' Handbook*, p. 241.

it indicates none but the "volatile" ammonia. If the test-acid is correctly made to contain 100 g. of H_2SO_4 per litre, each ounce used in the test is equal to 0·3469 oz. of NH_3 per gallon, or 0·217 part NH_3 by weight per 100 parts liquor by volume.

The estimation of ammonia in the presence of *pyridine bases* is described lower down.

2. *Estimation of Total Ammonia.*

(a) *Methods for the Use of Workmen.*—Knublauch (as quoted by Arnold, *Ammoniak und Ammoniakpräparate*, Berlin, 1888, p. 29) has worked out a simple testing-method for total ammonia in gas-liquor, intended to be used at small works where no chemist is employed, and he has constructed an apparatus for this purpose, sold by the designation "Ammoniakprober," by Messrs Leybold's Nachfolger, Cologne. His process is carried out as follows: 100 c.c. of the gas-liquor is diluted to 500 c.c., after having added a few pieces of caustic lime. Shake well up, allow to stand for an hour, and filter 50 c.c. of the liquid into a beaker, adding a little rosolic acid as indicator. From a graduated cylinder add semi-normal acid, until a red colour appears. If the cylinder had been filled up to the mark, the cubic centimetres used for the titration correspond to the percentage of ammonia in the gas-liquor, taking regard of the fact that in the 50 c.c. of dilute liquor there is as much lime dissolved as corresponds to 7·4 c.c. of semi-normal acid. It is asserted that this test is accurate up to 0·1 or 0·2 per cent.

Lubberger (*J. Gasbeleucht.*, xlii., p. 1; *Z. angew. Chem.*, 1899, p. 109) found that the necessary allowance for lime is quite different for different gas-liquors. He therefore proceeds as follows:—Distil 10 c.c. gas-liquor with lime, placing 30 c.c. seminormal acid into the receiver, and titrate back with seminormal alkali. Dilute 10 c.c. of the same gas-liquor with distilled water up to 200 to 300 c.c., tint it yellow by a few drops methyl-orange, and from a burette add seminormal sulphuric or hydrochloric acid (*not* oxalic acid!), until the colour changes to red. It is not necessary to boil the liquid. The difference between the acid used in the first and the second test is equal to the cubic centimetres seminormal acid, corresponding to the fixed ammonia. Make about eight such tests with gas-liquor of different days and weeks, take the average of the differences, and add it to the acid used in direct titration, since experience shows that the percentage of fixed ammonia is nearly constant. When using 10 c.c. of gas-liquor, each cubic centimetre of seminormal acid indicates 0·85 g. per litre. The burette should be every time filled up to the zero mark, and a table should be drawn up showing the cubic centimetres of acid used, and the corresponding percentage of ammonia.

Herting (*J. Gasbeleucht.*, 1900, p. 8) points out that this method cannot be used in all cases, *e.g.*, not for gas-liquor from Zwickau coal, since sometimes the percentage of fixed ammonia is very high and unequal.

(b) *Accurate Method* (*Distillation Test*).—The sample of liquor or salt is distilled with caustic soda, lime, magnesia, or baryta, and the vapours are passed either into water, or better at once into standard sulphuric acid, the unsaturated acid being afterwards determined by standard alkali (*cf.* conclusion of this chapter). Some prefer lime, baryta, or magnesia to the alkalis, on the (unfounded) assumption that the former are preferable, not splitting up organic alkaloids, while equally producing ammonia.

I have shown (*J. Soc. Chem. Ind.*, 1883, p. 514) that lime, magnesia, or soda in excess liberate equally well all the ammonia from ammonium chloride (and hence, presumably, all the "fixed" ammonia); but the distillation ought not to last less than three hours, otherwise the ammonia is not totally expelled. Hence, in analyzing pure ammonium salts it is indifferent which of the three fixed bases is employed, and caustic soda, being the simplest and cleanest to use, is preferable to the others. The compound ammonias and other organic bases behave exactly like ammonia; they are liberated under these circumstances by either soda, lime, or magnesia, and there is no advantage to be derived from employing the latter. Lime or soda, on distilling them for three hours with an excess of ammonium chloride, liberate their full equivalent of NH_3; but magnesia, on distilling for three to five hours, only about 85 per cent. of the theoretical quantity of NH_3, possibly owing to the formation of a basic magnesium chloride difficult to decompose. Hence magnesia must always be employed in excess. For practical purposes it must be considered that the ammonia manufacturer does not treat his liquors with magnesia, but with lime, and that hence the latter indicates the yield to be expected better than the former. Berthelot and André (*Bull. Soc. Chim.*, xlvii., p. 835) have proved that certain ammonium salts are not at all decomposed by magnesia, even on boiling, and only partially by lime, while soda decomposes them entirely.

The distillation test is very conveniently performed in the apparatus shown in Fig. 251. A is a flask, provided with a funnel-pipe closed by a pinchcock, for running in the caustic-soda solution; *b* is the gas-delivery pipe, provided with a bulb and cut off obliquely below, connected with the receiver B. The latter is connected with the safety-tube *c*, dipping into the beaker C, to prevent accidental loss by spurting over of standard acid.

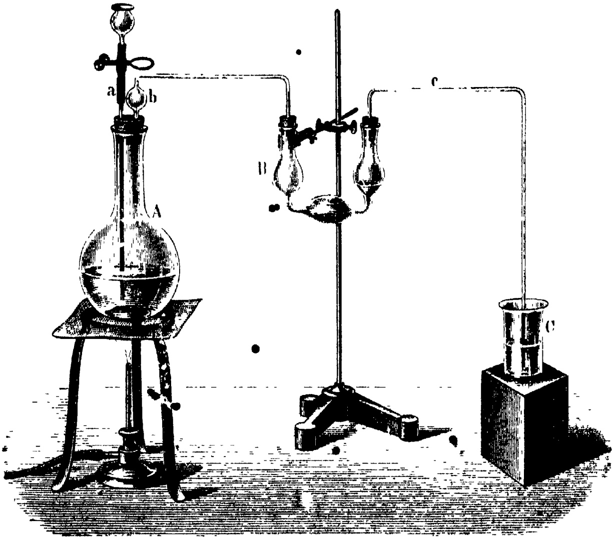

FIG. 251.

At some works they dispense with the funnel-tube *a*, and even with the U-tube B, employing an open flask as receiver. The flask A should hold about 400 c.c.; it is charged with

25 c.c. of gas-liquor, to which is added 50 to 150 c.c. water and about 50 c.c. milk of lime; the cork is quickly inserted, and thus the connection made with the receiving-tube or flask, already charged with very dilute standard acid. The liquor in A is gradually heated to boiling, which is continued by a small flame, afterwards increased; it is unnecessary to cool the receiver. The distillation is sometimes interrupted after an hour; but this does not seem quite enough, and it is better to carry it on for three hours.

In any case we would insist that the analyst convinces himself of the complete expulsion of the ammonia, by suspending, at the close of the distillation, a moistened piece of turmeric or other test-paper in the distillation vessel above the liquid. If this indicates any alkalinity whatever, the test must be repeated.

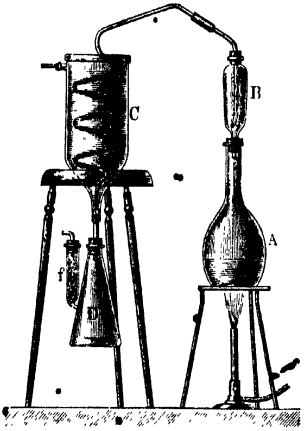

FIG. 252.

Stein and Schwarz (*Z. angew. Chem.*, 1889, p. 318) prevent the carrying over of alkali by the arrangement shown in Fig. 252. The vapours from the flask A pass in B through the lateral holes of the inner tube to the cooler C. The part *f* of the receiver D contains glass beads moistened with standard acid.

Milne (*J. Soc. Chem. Ind.*, vi., p. 423) employs magnesia in the following way:—A 250 c.c. flask is closed by an indiarubber cork through which passes a drop-funnel and a somewhat wide glass tube, leading to a cooler and a receiver charged with standard acid. The flask is charged with the substance to be tested together with 2 g. magnesia and (in the case of salts) 60 c.c. water. It is heated till its contents are nearly dry; then 10 c.c. of water is run through the drop-funnel, the boiling is continued, and this is repeated several times; at last air is aspirated through the apparatus before retitrating the acid.

E. Henry (*Bull. Soc. Chim.* [3], ix., 1018), in the case of gas-liquor containing much sulphide and cyanide, adds a little basic acetate of lime before distillation.

The following details of the process have been found most suitable at the large works of Kunheim & Co., near Berlin. The bulk-sample is well ground up, the whole of it passed through a sieve with about 8 meshes per linear inch, and a small sample taken from it. Of this liquor about 15 g. are weighed out, and are dissolved to 500 c.c.; 50 c.c. of this are introduced without filtering into a 300-c.c. flask and distilled with about 15 c.c. caustic-soda solution of sp. gr. 1·25 for three hours; the evolved gas is absorbed in 50 c.c. of seminormal standard acid, and titrated back with seminormal soda solution and litmus till purple.

Oxalic acid has been frequently recommended as standard acid, but not justly. It is difficult to obtain it perfectly pure, and impossible to make sure that it contains neither too much nor too little water; hence the acid must always be tested in other ways; and when using it methyl-orange and several other indicators cannot be employed.[1] It is therefore best to employ at once, as cheaper and more stable, *sulphuric* or *hydrochloric acid*. The latter is preferable, since its strength can be exactly estimated in two different ways, viz., by titrating a known weight of freshly ignited pure sodium carbonate, or gravimetrically by means of silver nitrate. The standard acid is either made normal, so that 1 c.c. contains 0·04904 g. SO_4H_2 or 0·03646 HCl, and indicates 0·01703 g. NH_3, or else it is made one-half, one-fifth, or one-tenth of that strength.

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[1] Bruhns (*Z. anal. Chem.*, 1916, pp. 23 *et seq.*) found methyl-orange to be perfectly suitable for titrating oxalic acid, if at least the equivalent proportion of calcium chloride is added.

The standard acid is kept in large bottles protected from great changes of temperature; whenever smaller stock-bottles or the burettes are to be filled with it, the large bottle ought to be shaken in order to mix its contents with any moisture evaporated, and again condensed in the empty upper part of the vessel. As standard alkali for retitrating the acid partly saturated by the evolved ammonia, some chemists prefer ammonia or caustic baryta to caustic potash or soda; but ammonia solutions are not sufficiently stable, and baryta solution (which is often used in agricultural laboratories) is much more troublesome to handle than soda or potash.

Far preferable to litmus as an indicator is *methyl-orange.* For retitrating a solution of soda or potash can be employed without any special precautions against attracting carbonic acid, since this does not interfere with the delicacy of the test; and thus titration with caustic potash or soda, with methyl-orange as indicator, is the most convenient of the methods described.

L. W. Winkler (*Z. angew. Chem.*, 1913, i., p. 231; 1914, i., p. 630) absorbs the ammonia by *boric acid.* He passes the ammonia, distilling over as described *supra*, into 100 c.c. water containing 10 g. crystalline boric acid, with good cooling, and titrates back with decinormal or fifth-normal hydrochloric acid, employing as indicator methyl-orange or congo-red. Bernard (*ibid.*, 1914, i., p. 664) strongly recommends this method.

(c) *Azotometric Test.*—This is founded on the fact that a solution of sodium hypochlorite containing bromine, or of sodium hypobromite, in the presence of a large excess of alkali almost instantaneously liberates all the nitrogen of ammonia salts. Such a solution is made by dissolving 100 g. of caustic soda in 250 c.c. of water, cooling the liquid (best by ice), and running in, with constant stirring, 25 g. of bromine. This solution does not keep very long, but it is decomposed, oxygen being given off.

The azotometer mostly used is that of Knop, modified by Wagner (Fig. 253). A is the flask for receiving the brominated soda, holding 200 c.c., with an inner tube, *a*, sealed to its bottom. The neck of A is ground, to prevent the indiarubber cork from slipping. B is a glass vessel holding about 4 litres of water; C a cylinder filled with water and a little hydrochloric acid (to prevent the growth of fungi), with a wooden lid through which pass the two burettes *c* and *d* and a small thermometer. *h* is a vessel communicating with the burettes by tap *g*, and filled, like these, with coloured water.

To make an analysis, *e.g.*, of ammonium sulphate, 10 g. of this are dissolved in 500 c.c. water, and 100 c.c. of this solution =0·2 g. of sulphate is introduced into *a*, 50 c.c. of bromine solution are placed in the outer space of A, the cork is put tightly in and the flask placed in the water-vessel B. Tap *f* is slightly loosened, tap *g* is opened, and by compressing the indiarubber ball *i* the burettes *c* and *d* are filled; by regulating at *g* the level of the liquid is placed at zero. After ten minutes' waiting, tap *f* is put in tight, but kept open to see whether

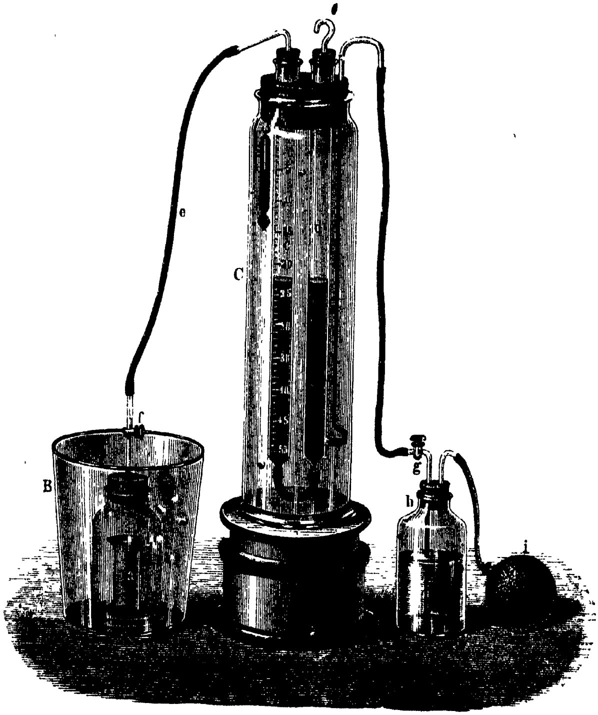

FIG. 253.

the level in c rises: if it does not rise within five minutes, the contents of A have assumed the temperature of the water in B. Now about 30 or 40 c.c. water are run out of g, A is taken out of B and inclined so that some of the ammonia solution mixes with the bromine solution, the flask is shaken, and this is repeated until the liquids are completely mixed and no more gas is evolved. Then A is again placed in B and left for fifteen or twenty minutes to assume the temperature of the water-bath. The levels of c and d are now equalized by running water out of g, and the volume of gas contained in c is read off, together with the temperature of the water in C and the barometric pressure.

The volume of gas read off is reduced to 0° and 760 mm. pressure by the formula:

$$V_1 = \frac{273V(b-f)}{(273+t)760},$$

in which b is the barometric pressure (in millimetres), f the tension of aqueous vapour at the temperature t, t the temperature of the water in C. This calculation can be simplified by tables, such as those calculated by myself, by Cl. Winkler, and others. It is also dispensed with by employing, in lieu of the azotometer, the "gas-volumeter" constructed by me (*cf.* my *Sulphuric Acid and Alkali*, 4th ed., vol. i., p. 383, or my *Technical Chemists' Handbook*, 1910, p. 217), in which the gas is mechanically reduced to 0° and 760 mm. pressure.

Each cubic centimetre of nitrogen, reduced to normal conditions, corresponds to 0·001254 mg. N or 0·0015246 mg. NH_3. These figures would, however, give a wrong result if used for the azotometric operation without correction, a certain "absorption" of nitrogen taking place, or rather the reaction not being complete.

A correction must be applied on this account, according to the subjoined table, experimentally determined by E. Dietrich for the case in which 60 c.c. of liquid (50 of brominated soda and 10 of water) are used, of such strength that it is capable of liberating 200 c.c. of nitrogen. This table shows the number of cubic centimetres to be added to the quantity found, when this quantity ranges from 1 to 100 c.c.

Correction for the Volume of Gas found by the Azotometric Method.

Found.	Add.	Found.	Add.	Found.	Add.	Found.	Add.	Found.	Add.
c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
1	0·06	21	0·56	41	1·06	61	1·56	81	2·06
2	0·08	22	0·58	42	1·08	62	1·58	82	2·08
3	0·11	23	0·61	43	1·11	63	1·61	83	2·11
4	0·13	24	0·63	44	1·13	64	1·63	84	2·13
5	0·16	25	0·66	45	1·16	65	1·66	85	2·16
6	0·18	26	0·68	46	1·18	66	1·68	86	2·18
7	0·21	27	0·71	47	1·21	67	1·71	87	2·21
8	0·23	28	0·73	48	1·23	68	1·73	88	2·23
9	0·26	29	0·76	49	1·26	69	1·76	89	2·26
10	0·28	30	0·78	50	1·28	70	1·78	90	2·28
11	0·31	31	0·81	51	1·31	71	1·81	91	2·31
12	0·33	32	0·83	52	1·33	72	1·83	92	2·33
13	0·36	33	0·86	53	1·36	73	1·86	93	2·36
14	0·38	34	0·88	54	1·38	74	1·88	94	2·38
15	0·41	35	0·91	55	1·41	75	1·91	95	2·41
16	0·43	36	0·93	56	1·43	76	1·93	96	2·43
17	0·46	37	0·96	57	1·46	77	1·96	97	2·46
18	0·48	38	0·98	58	1·48	78	1·98	98	2·48
19	0·51	39	1·01	59	1·51	79	2·01	99	2·51
20	0·53	40	1·03	60	1·53	80	2·03	100	2·53

Excepting the first few cubic centimetres, this table can be practically dispensed with by putting each cubic centimetre of gas read off=0·0012818 N or 0·0015582 NH_3.

The azotometric method is more adapted for the estimation of smaller quantities of NH_3 in fertilizers, etc.; for the analyses of commercial sulphate of ammonia the distillation test (pp. 1270 *et seq.*) is preferable. For raw gas-liquor it is not at all adapted, since the brominated liquor reacts on other organic constituents of this, and thus abnormally high results are produced. (Donati and Pollak, *Z. angew. Chem.*, 1897, p. 555.)

Sara S. Graves (*J. Amer. Chem. Soc.*, 1915, xxxvii., p. 1171) precipitates ammonia by a mixture of mercuric chloride, sodium chloride, and lithium carbonate.

Complete Analysis of Ammoniacal Liquor.

S. Dyson (*J. Soc. Chem. Ind.*, 1883, p. 229) describes the following methods for a complete analysis of gas-liquor, taking, however, no account of organic bases and other substances difficult to estimate.

(a) *Determination of Total Ammonia.*—Twenty-five c.c. of the liquor is boiled with magnesia, and the evolved ammonia collected in 50 c.c. standard sulphuric acid, which is afterwards titrated back with standard soda. Suppose this showed 2·045 per cent. NH_3. [Dyson prefers magnesia to lime, because in a check experiment, where he distilled the liquor with lime almost to dryness, 2·152 per cent. NH_3 was obtained, which he, no doubt rightly, attributes to the action of lime on organic substances containing nitrogen. This action of the lime can be easily avoided by employing a more dilute solution, and not boiling to dryness. When employing magnesia, it must not be forgotten that its action is much less energetic and slower than that of lime (*cf.* p. 1270).]

(b) *Determination of Total Sulphur.*—Twenty-five c.c. of the liquor are allowed to fall, drop by drop, from a burette into water, acidulated with hydrochloric acid and containing some free bromine. The excess of bromine is evaporated off, the solution filtered from the precipitate formed (which seems to consist mainly of tribromophenol), and the sulphur precipitated as barium sulphate. This yields, we suppose in a special case, 0·3915 per cent. S.

(c) *Determination of Sulphides.*—Zinc sulphate and ammonium chloride are added to 25 c.c. liquor; the precipitate is filtered off and well washed. The filter-paper is perforated, and small portions of the precipitate are gradually washed through into water acidulated with hydrochloric acid, and containing an excess of bromine. When the whole of the precipitate has been washed through, the solution is heated to expel the excess of bromine, filtered, and barium chloride added to the filtrate. Suppose we obtain thus 0·190 per cent. $S = 0{\cdot}303\ NH_4.HS$.

(d) *Determination of Carbonates.*—An ammoniacal solution of calcium chloride is added to 25 c.c. liquor. The precipitated calcium carbonate is filtered off, dissolved in 50 c.c. standard hydrochloric acid, and the solution titrated back with standard soda. Suppose we thus obtain 1·795 per cent. $CO_2 = 3{\cdot}916\ (NH_4)_2CO_3$.

(e) *Determination of Chlorides.*—Fifty c.c. are evaporated to dryness on the water-bath. [This might lead to some sal-ammoniac being volatilized!] Water is added, and the undissolved tarry matters filtered off. The filtrate is mixed with a solution of copper sulphate and ferrous sulphate in about equal proportions (in order to remove thiocyanates) and the liquid again filtered. Nitric acid and silver nitrate are added to the filtrate and the solution is boiled. The precipitate is allowed to settle and the supernatant liquid poured through a filter. Before finally filtering off the silver chloride, it is digested several times with hot nitric acid, to dissolve out the silver sulphide resulting from the decomposition of the silver thiosulphate. [This might easily lead to some AgCl being dissolved! Cf. *infra*, Herting.] The silver chloride is then filtered off and weighed. Suppose we obtain 0·944 Cl = 1·1423 NH_4Cl.

(f) *Determination of Thiocyanate* (*Sulphocyanide*).—This is not very easy, and is best done in the following way:—Fifty c.c. of the gas-liquor are evaporated to complete dryness, and the residue is heated to 100° for three or four hours, in order to make the precipitate of thiocyanate to be obtained later on less finely divided. The residue is then digested with strong alcohol, rinsed on to a filter, and washed with alcohol. The alcoholic filtrate is evaporated to dryness, water is added and the insoluble organic matter filtered off. A solution of ammonium thiocyanate is thus obtained, tolerably free from other ammoniacal salts (especially thiosulphate) and from organic matter. This solution is precipitated by the addition of cupric sulphate and sulphurous acid (which is preferable to ferrous sulphate as a reducing agent); it is gently warmed (not boiled!) and, after settling, the cuprous thiocyanate, CuCNS, is filtered off. It is then washed into a flask, dissolved in nitric acid, and the liquid boiled for a considerable time. The copper is then precipitated as oxide by caustic soda; the weight of $CuO \times 0{\cdot}96$ = the equivalent amount of NH_4CNS. Suppose we obtain 0·180 NH_4CNS. [The volumetric method of Liddle and Barnes (*J. Soc. Chem. Ind.*, 1883, p. 122) was found by Dyson to be inapplicable to gas-liquor. But Linder (*Thirty-ninth Alkali Report*, for 1902, pp. 229-231) holds that Dyson's method for the estimation of thiocyanate is not trustworthy.]

(g) *Determination of Sulphates.*—Two hundred and fifty c.c. are evaporated to dryness. Water is added, the organic substances filtered off, and the solution boiled with HCl. A little zinc oxide is added, the liquid filtered, and the sulphates precipitated with barium chloride. Suppose we obtain 0·019 per cent. $(NH_4)_2SO_4$.

(h) *Determination of Thiosulphates.*—This cannot be done by any direct method; but it may be arrived at by subtracting from the amount of total sulphur that existing as sulphides, thiocyanates, and sulphates. In our example:—

Total sulphur		0·3915
Sulphur in sulphides	0·1900	
„ thiocyanates	0·0757	
„ sulphates	0·0046	
		0·2703
Sulphur in ammonium thiosulphate		0·1212

=0·280 per cent. $(NH_4)_2S_2O_3$.

(i) *Ferrocyanides.*—The residue obtained by evaporating 250 c.c. of the liquor to dryness is dissolved in water, the solution filtered, and ferric chloride added to the filtrate. The precipitate of Prussian blue is filtered off, washed, and decomposed by caustic soda. The ferric hydroxide thus obtained is, after filtering and washing, dissolved in dilute sulphuric acid, reduced, and the solution titrated with centinormal potassium permanganate. The Fe × 5·07 equals the amount of $(NH_4)_4FeCy_6$. Suppose we have found 0·0415 per cent. of this compound.

The result will therefore be that 1 litre of the sample of gas-liquor analyzed contains in grams:—

Total ammonia	20·45		
„ sulphur	3·92		
Ammonium sulphide, NH_4HS	3·03	=	1·01 NH_3.
„ monocarbonate, $(NH_4)_2CO_3$	39·16	=	13·87 „
„ chloride, NH_4Cl	14·23	=	4·52 „
„ thiocyanate, NH_4CNS	1·80	=	0·40 „
„ sulphate, $(NH_4)_2SO_4$	0·19	=	0·05 „
„ thiosulphate, $(NH_4)_2S_2O_3$	2·80	=	0·64 „
„ ferrocyanide, $(NH_4)_4FeCy_6$	0·41	=	0·10 „
			20·59

Herting (*Schilling's J.*, 1900, p. 206) confirms my doubts as to the accuracy of the estimation of chlorine, *suprà*, at (c). He proceeds as follows:—Dilute 10 c.c. gas-liquor to 250 c.c., take out 50 c.c., add a few cubic centimetres nitric acid, decompose the ammonium sulphide and carbonate by boiling, precipitate by an excess of silver nitrate, collect the AgCl, wash it on the filter with hot water, dissolve it on the filter by ammonia (the tarry substances remain behind), acidulate the filtrate with nitric acid, boil up, collect the pure AgCl on a filter, ignite with the usual precautions, and weigh. Titration of the chloride with decinormal silver solution is not feasible, as the potassium chromate indicator does not work in this case.

Cf. also in Chapter XV. the methods employed for the examination of commercial liquor ammoniæ.

A great many valuable contributions to this chapter have been made by the inspectors under the Alkali Acts, and are recorded in their reports.

In the *Alkali Report*, 1896, p. 23, the remark is made that the estimation of *thiosulphates* by iodine is difficult in gas-liquor owing to the presence of phenols. It is therefore best to proceed as follows:—Add an excess of zinc sulphate and enough acetic acid to dissolve most of the zinc carbonate. Filter the ZnS, wash with water of 60° or 80°, pierce the filter and wash its contents into an excess of decinormal iodine adding 2 c.c. concentrated hydrochloric acid, and washing the filter with a little dilute hydrochloric acid. Titrate back with decinormal thiosulphate, and calculate the thiosulphate in the gas-liquor from the difference between the total sulphur and that of the sulphide, sulphate, and thiocyanate. According to the same source, the estimation of *chlorides* is performed as follows:—Dilute 10 c.c. gas-liquor, expel the volatile matters by prolonged boiling, dilute to 100 c.c., add 10 c.c hydrogen peroxide solution, and boil twenty minutes, replacing the water evaporated; add potassium carbonate till the reaction is neutral, boil till the brown-red colour has disappeared, clear up by means of a little sodium bicarbonate, and titrate the cooled liquor with standard silver nitrate.

The *Thirty-sixth Alkali Report*, for 1899, pp. 47 *et seq.*, describes the methods of analysis employed by the chief inspector, Mr R. Forbes Carpenter. These differ from former methods principally as follows:—The thiosulphate is estimated by diluting the filtrate from the mixed zinc sulphide and carbonate, adding a few drops of strong hydrochloric acid, and titrating forthwith with $N/10$ iodine and starch, taking the *first* appearance of a definite blue colour as the end of the oxidation of thiosulphate to tetrathionate.

The analytical methods employed by Mr Linder (whose tables are given on pp. 1259 *et seq.*) are fully described in the *Fortieth and Forty-sixth Report on Alkali, etc., Works*, for 1903, pp. 31 *et seq.*; for 1909, pp. 15 *et seq.* They may be summarized as follows:—

1. *Ammonia.—Volatile Ammonia* (*a*) by direct titration with *N*/2 sulphuric acid and methyl-orange, to determine approximately the volume of acid required for (*b*). (*b*) Dilute 10 c.c. liquor (more if weak) to 30 c.c. in a round-bottomed flask with catch-bulb, Liebig's condenser and receiver. Distil into a receiver, containing excess of *N*/2 sulphuric acid, provided with outlet acid catch, packed with broken Jena glass. Distil 150 c.c., titrate back the excess of acid in receiver, then distil 100 c.c. into a receiver without acid (the amount of NH_3 in this portion is generally *nil*).

Fixed Ammonia.—Add boiled caustic soda in excess, with sufficient water to replace that distilled off, and proceed as above.

2. *Carbonic Acid.*—Dilute 10 c.c. to 400 c.c., add 10 c.c. of ammoniacal calcium chloride (1 c.c. = 0·044 g. CO_2), heat in a stoppered bottle for one and a half to two hours in a water-bath at 100°, cool, filter, wash, dissolve the $CaCO_3$ in *N*/2 HCl.

3. *Chloride.*—Dilute 10 c.c. of boiled liquor to 150 c.c., add 20 c.c. of hydrogen peroxide free from chloride, boil until the brown colour has almost entirely disappeared, add 10 to 15 drops K_2CrO_4 solution, boil for five minutes, cool, neutralize by sodium bicarbonate, and titrate with *N*/10 $AgNO_3$.

4. *Sulphur* (a) *as Sulphate.*—Concentrate 250 c.c. of liquor to about 10 c.c. on the water-bath, add 2 c.c. strong hydrochloric acid, evaporate to dryness to decompose thiosulphate, extract the residue with water, filter, and precipitate the solution with barium chloride.

(b) *As Sulphocyanide* (Thiocyanate).—To 50 c.c. of the boiled solution add ferric chloride in slight excess to precipitate the ferrocyanide as Prussian blue, warm up the solution, filter, cool, add SO_2 solution in sufficient excess, followed by cupric sulphate, allow to stand in stoppered flask for one to two hours, filter cold, wash the cuprous sulphocyanide thoroughly on the filter, wash it back into the flask, boil with 1 c.c. strong nitric acid until green, cool, add slight excess of sodium carbonate, acidify with acetic acid, add a dilute solution of potassium iodide, and titrate the liberated iodine with *N*/10 thiosulphate and starch (details in *Thirty-ninth Alkali Report*, for 1902, pp. 71-74).

(c) *As Sulphide, Sulphite, and Thiosulphate.*—(1) Titrate 10 c.c., after dilution to 500 c.c., acidified with HCl, with iodine and starch.

(2) Add 10 c.c. of liquor to excess of ammoniacal zinc chloride solution, filter, wash the ZnS on the filter with warm water, wash it off the filter into excess of *N*/10 iodine, acidified with HCl, and determine the excess iodine with *N*/10 thiosulphate. The sulphite and thiosulphate are found by subtracting the sulphide found as above from the figure obtained in (1).

(d) *Total Sulphur.*—Deliver 50 c.c. drop by drop from a burette into a flask containing excess of bromine, covered by water strongly acidulated with HCl, evaporate to dryness, extract the residue with boiling water, and precipitate the filtrate with barium chloride.[1]

(e) *Polysulphide* cannot exist in ordinary ammoniacal liquors, since it reacts with sulphites and cyanides.

Mayer and Hempel (*J. Gasbeleucht.*, 1908, pp. 381, 403, 425) employ the following methods :—*Ammonia* (a) *volatile*, is estimated by diluting with 10 times the amount of water, distilling and titrating the distillate; (b) *fixed*, by redistilling the residue with caustic alkali or lime; *carbon dioxide*, by adding ammoniacal $CaCl_2$, heating for two hours, cooling, filtering, and washing the $CaCO_3$ in a good crucible and titrating; *chloride* and *sulphide*, by Linder's methods (*supra*, p. 1282); thiosulphate, by adding an excess of the chlorides of strontium, zinc, and ammonia, washing the precipitate with dilute solution of strontium chloride, acidifying the filtrate and titrating the thiosulphate by means of iodine solution. To determine the *sulphite*, the acidified gas liquor is titrated in the same way, and the sulphide and thiosulphate, obtained as above, are deducted, obtaining the sulphite by difference; *thiocyanate*, by Linder's method (*supra*, p. 1282); *sulphate*, by boiling down with hydrochloric acid, extracting the residue with hot water, and precipitating the acidified filtrate with barium chloride; *total sulphur*, as in Dyson and Linder's methods (*supra*, p. 1283); *cyanide* and *ferrocyanide*, as below.

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[1] In *Chem. Tech. Unt. Meth.*, 5th ed., ii., 705, I recommend to acidulate the liquid only slightly, not strongly, to avoid an escape of H_2S. Treadwell (*Anal. Chem.*, 2nd ed., ii., 338) recommends employing as little potassium salts as possible in decomposing the bromine compounds. Mayer and Hempel (*J. Gasbeleucht.*, 1908, p. 425) confirm both these recommendations.

The processes for analysing ammoniacal liquor, described by Pfeiffer (Lunge's *Methods of Technical Analysis*, translated by Keane, 1911, vol. ii., part 2, pp. 733 *et seq.*) agree in all essential points with those described by Dyson and by Mayer and Hempel (*vide supra*).

Special Methods for Sulphides, Cyanides, Phenols, etc.

W. Feld has published papers on the determination of sulphides, sulphides and thiosulphates (*Chem. Ind.*, 1898, p. 372; *J. Soc. Chem. Ind.*, 1898, p. 1186) and on mixtures containing, in addition to these bodies, thiocyanate and cyanogen compounds in general (*J. Gasbeleucht.*, xlvi., 1903, pp. 561 and 660; *J. Soc. Chem. Ind.*, 1903, p. 1068). A thorough examination of these methods with partly unfavourable results was made by Linder (*Forty-first Alkali Report*, for 1904, pp. 27-36).

Mayer and Hempel (*J. Gasbeleucht.*, 1908, p. 426) modify Feld's method for estimating the *cyanide* as follows:—They distil 250 c.c. gas-liquor, after adding a sufficient quantity of 20 per cent. solution of lead nitrate to keep back the H_2S; the distillate is taken up in 25 cbm. standard caustic-soda solution, to which 5 c.c. standard KI solution has been added as indicator. Such a distillation takes about half an hour.

The same authors declare Feld's method for estimating the *ferrocyanide* to be the only practicable one. They carry it out as follows:—250 (or 500) c.c. gas-liquor are placed in a covered glass dish and are just acidified. Then add a solution of iron-ammonia alum until a permanent red colour has been produced, heat to 60°, allow to cool, filter through a plaited filter, wash two or three times with water containing sodium sulphate, place the filter in a distilling-flask, heat for five or ten minutes with 3 to 5 c.c. of 8-normal caustic-soda solution, add 35 c.c. of 3-normal solution of magnesium chloride, stir up and add to the boiling solution 100 c.c. of a boiling $N/10$ solution of mercuric chloride. After boiling for a quarter of an hour the decomposition is finished, a light brown precipitate has been formed, and the liquid is quite clear. Now connect with the cooler and distil the HNC off in the usual manner.

Carpenter and Linder (*J. Soc. Chem. Ind.*, 1904, p. 585) estimate *hydrocyanic acid* in ammoniacal liquors by distilling the liquor with excess of tartaric acid into caustic soda in an apparatus provided with receiver and Liebig's condenser, similar to that employed for the estimation of fixed ammonia (*supra*, p. 1282), lead nitrate being added in excess to retain the sulphide, and ferric chloride to convert any ferrocyanide present into Prussian blue, a substance which evolves no hydrocyanic acid under the observed conditions. The cyanide obtained in the distillate is determined by titration with decinormal silver nitrate or decinormal iodine in the usual way.

The *phenols* in gas-liquor are determined by Skirrow (*J. Soc. Chem. Ind.*, 1908, p. 58) by a modification of the well-known method of Messinger and Vortmann (*supra*, p. 802), viz., distilling them off with water, converting them into tri-iodophenol by means of an excess of iodine and titrating back with thiosulphate. In the present case the sulphides and cyanides must be previously removed, and the liquor on evaporation must be permanently and strongly alkaline. One hundred c.c. of the filtered gas-liquor is treated with an excess of ammonium polysulphide, to convert any cyanide present into thiocyanate. The solution is made up to 200 c.c., the sulphides are precipitated by lead carbonate. To 100 c.c. of the filtered solution, 25 c.c. of a 50 per cent. solution of sodium hydroxide is added and the whole evaporated until the salts begin to separate; the residue is washed into a litre distilling-flask and diluted to about 150 c.c. with distilled water, and when cold, acidified with sulphuric acid. The liquid is distilled until the salts begin to crystallize out; we thus obtain "distillate 1." One hundred c.c. is added in the distilling flask, and the liquor again distilled into a second receiver, giving "distillate 2." This is repeated a third time, giving "distillate 3." Each of these distillates is shaken with about 1 g. of calcium carbonate and a little lead carbonate (to get rid of any acid and sulphides carried over), and redistilled. In doing this, No. 1 is distilled first, No. 2 is then added to the flask and distilled, No. 3 being distilled last.

The final distillates are united and made up to 500 c.c. One hundred c.c. of this are made alkaline with NaOH, warmed to 60° C., an excess of iodine run in, the flask immediately stoppered and cooled with frequent shaking. Then the solution is acidified and titrated back with one-tenth normal sodium thiosulphate, starch being used as indicator. About 4 mol. of NaOH to each mol. of phenol should be used in the previous neutralization, to produce a sharp transition from blue to pink, and for this purpose a preliminary test is made, and followed by a final test. The reaction is:—

$$C_6H_5OH + 6I = C_6H_2I_3OH + 3HI.$$

On acidification the excess of iodine, which had passed over into $NaIO + NaI$, is set free:

$$NaIO + NaI + H_2SO_4 = Na_2SO_4 + H_2O + I_2,$$

and can be titrated.

Skirrow quotes a large number of estimations made in this way, showing generally 0·2 to 0·3 g. phenol per 100 c.c. of gas-liquor, and 0·1 to 0·19 g. in coke-oven liquor. A further examination showed that the phenols in gas-liquor contain about 65 per cent. of pure phenol and 35 per cent. of cresols, etc., owing to the fact that pure phenol has more strongly acid properties than its homologues, and is therefore more easily taken up by the ammoniacal liquor. As the quantity of phenols obtained from the coal-tar amounts to about 0·24 kg. per ton of coal, there is nearly as much phenol lost in the gas-liquor, which cannot be expected to be turned to any account.

Pyrocatechine was found by Börnstein (*Ber.*, 1902, p. 4324) in the ethereal extract from the aqueous distillate, obtained by distilling coal at a very low heat.

The estimation of *pyridine* in ammoniacal liquor is important for the manufacture of anhydrous ammonia intended for ice-producing machines, since the pyridine causes very much trouble in the ammonia compressors. Pyridine, according to Pinchbeck (*Pharm. J.*, 1909, p. 84; *J. Soc. Chem. Ind.*, 1909, p. 202), is detected in ammoniacal liquor as follows:—Dilute 50 c.c. of the liquor, neutralize with HCl, render alkaline with NaOH, and shake with 10 c.c. chloroform. To one-half of the chloroform extract add 0·25 c.c. strong hydrochloric acid and 2 drops of a solution of bromine in chloroform. In the presence of a small quantity of pyridine, a crystalline bromo-compound, $C_5H_4Br_2$, is precipitated. The other half of the extract is exposed to a current of warm air; the residue left will have the characteristic odour of pyridine, if this be present. For a quantitative estimation, 100 c.c. of the ammoniacal liquor, diluted with 100 c.c. water, is neutralized with sulphuric acid, rendered alkaline with NaOH, diluted to 400 c.c., and distilled until one-third has passed over. The distillate is treated with 10 g. mercuric chloride, dissolved in 150 c.c. water, the precipitate filtered and washed with cold 92 per cent. alcohol, which dissolves the compound of pyridine with $HgCl_2$. This solution is neutralized, diluted to 400 c.c., and slowly distilled. The distillate should not require for neutralization (indicator: methyl-orange) more than 2 c.c., one-tenth normal NaOH, equal to 0·00948 per cent. pyridine.

A. Bayer (*J. Gasbeleucht.*, 1912, p. 513) points out that for the titration of pyridine in ammoniacal solutions litmus and phenolphthalein are useless. Methyl-orange can be employed if the titration is made from acid to alkaline reaction by means of barium hydrate; the indicator must be put into the acid solution only up to a faint pink colour, and the baryta solution must be added until the colour of the solution, after thorough agitation, is golden yellow, without any shade of pink. A very good indicator in this case is *ferric sulphocyanide*, applied in the following way:—To the liquid containing free ammonia or pyridine are added a few drops of a solution of 0·75 g. ferric chloride in 250 c.c., and a solution of 6 g. ammonium sulphocyanide in 250 c.c., then sufficient *N*/10 hydrochloric acid to produce an acid reaction; the red-brown liquid formed is neutralized by *N*/10 caustic-soda solution up to the point that all the ammonia or pyridine is converted into neutral salts, which at ordinary temperatures have no action on the ferric hydrate formed from the ferric sulphocyanide. Now *N*/10 caustic-soda solution is added up to the point that the liquid is altogether *colourless*, without any brownish shade. If pyridine is to be estimated in the presence of a great excess of ammonia, the well-known process is employed: distilling the liquid after having almost completely neutralized it with sulphuric acid (as indicated by litmus); and collecting a third of the liquid as distillate, which contains all the pyridine in a more concentrated form, together with a certain proportion of ammonia. In this distillate first the ammonia is titrated by means of *N*/10 acid, using litmus paper as indicator; then the litmus paper is removed, a suitable excess of acid is added, then both the indicator liquids described *supra*, and the excess of acid retitrated with *N*/10 caustic-soda solution.

Since the application of litmus paper frequently leads to mistakes by the slowness of the reaction, Bayer has introduced a modification of a method for estimating ammonia in the presence of pyridine, formerly described by him (*Chem. Zeit.*, 1903, p. 809), which yields quite correct results. It consists in precipitating the ammonia in the alkaline solution as ammonia-magnesia phosphate, whilst pyridine does not form such a double salt, and after filtering the solution from the precipitate is obtained by distillation as a pure aqueous solution, which can be titrated. The reagent for precipitating the ammonia is prepared by dissolving 2·5 g. caustic magnesia in hydrochloric acid as nearly as possible to neutralization, adding 25 g. crystallized disodium-phosphate and 50 g. citric acid, then a few drops phenolphthalein solution, and so much caustic soda that the reaction is barely acid, and ultimately diluting to 250 c.c. This solution is approximately one-fourth normal and keeps well. If this reagent is added to the distillate containing ammonia and pyridine, no matter whether this has been collected in acid or whether it is alkaline, and then caustic-soda solution is added, drop by drop, up to the point that a pink colour is just appearing, the secretion of the ammonia-magnesia phosphate at once sets in and is promoted by good stirring. As the ammonia is thus removed, the liquid turns acid; therefore a little more of the reagent and of caustic soda is added until the pink colour returns and remains. After agitating for an hour at the ordinary temperature, all the ammonia is precipitated. The precipitate is filtered with employment of the air-pump, and the precipitate left on the filter, which need not be washed with pure water, is put together with the filter into a distilling flask where the ammonia is distilled off after adding some water and magnesia. In order to estimate the pyridine contained in the filtered solution, this is distilled and yields an aqueous solution, entirely free from ammonia. It is caught in $N/10$ hydrochloric acid and titrated with the indicator solutions *supra* described.

By this method Bayer found the following quantities of ammonia and pyridine (grams per litre):—

	Ammonia.	Pyridine.
In crude gas-liquor	1·342	0·1669
In crude gas-liquor	1·025	0·1583
In the liquor condensed behind the cooler	23·54	3·1632
In liquor ammoniæ, sold as chemically pure . . .	25·15	0·1754
In liquor ammoniæ, technically pure	25·20	0·1063

Houghton (*J. Ind. Eng. Chem.*, 1908, i., p. 698) estimates pyridine in ammoniacal liquor after destroying the ammonia. He dilutes 100 c.c. of the liquor with 150 c.c. distilled water, neutralizes with dilute sulphuric acid (1 : 3) up to the change of colour of methyl-orange, adds 5 c.c. of $N/10$ soda solution and distils, making the vapours pass through 100 c.c. of a solution of sodium hypobromite (prepared by adding 25 c.c. bromine to a solution of 100 g. caustic soda in a litre of water), and then through $N/10$ acid. The ammonia is destroyed by the hypobromite solution with liberation of nitrogen, so that the $N/10$ acid takes up only the pyridine, the quantity of which is found by retitrating the acid. Each cubic centimetre of acid = 0·0079 g. pyridine.

In cases where the gas-liquor contains a large proportion of pyridine, Redwood agitates 100 c.c. of the liquor with 25 c.c. normal soda solution and 50 c.c. refined petroleum spirit, which by prolonged shaking takes up the pyridine bases, so that the ammonia can be titrated by itself in the aqueous liquid separated from the petroleum spirit.

Délépine and Sornet (*Bull. Soc. Chim.* [4], ix., p. 706) describe methods for separately estimating ammonia and pyridine by gold chloride, or platinum chloride, or mercuric chloride solution.

Examination of Concentrated Ammoniacal Liquor.

For this purpose the German Union for the Sale of Ammonia has given the following prescriptions.

The concentrated ammoniacal liquor should contain at least 14 per cent. ammonia. The percentage of ammonia is ascertained in the following way:—Two average samples are taken from the contents of each tank-wagon before sending it away. One of these is examined in the works' laboratory, and the result communicated to the buyer, who on his part examines an average sample and communicates the result to the Union. If the analyses are not concordant, any differences up to 0·5 per cent. are halved. Any greater differences are settled by mutual concessions, or else by the decisive analysis of the second sample, which had been retained at the ammonia works, made by a public laboratory, whose results are in any case binding for both parties. The costs of this analysis must be borne by that party whose results deviate most from it.

Estimation of Ammonia in Spent Oxide of Gas-works.

The percentage of ammonia in spent oxide, according to J. Carter Bell (*J. Soc. Chem. Ind.*, 1883, p. 110), is often returned in extremely varying quantity by different chemists, according to the method of analysis employed. He recommends the following method as being analogous to the manner in which the oxide can be worked up commercially:—If the oxide is poor in ammonia, 10 g. are heated in the water-bath till dry. This will give the moisture, and also drive off any volatile ammonia which cannot be profitably collected in practice. The oxide is then washed with boiling water till free from ammonia salts, filtered, and the washings put into a flask. Milk of lime is added, the contents of the flask are boiled, and the NH_3 is driven over into sulphuric acid. The certificate is made out as ammonia equal to sulphate; for in some cases so much sulphocyanide (thiocyanate) is present as to unfit the salt for manure-making. Bell supposes (but wrongly) that the sulphocyanide is not decomposed by lime, whilst it would be so by soda.[1] If, instead of the solution, the oxide itself were directly boiled with lime or soda, very much nitrogenous matter would be split up and would also yield ammonia, which would falsify the test.

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[1] I cannot otherwise understand his expression—"Even if the ammoniacal salts are washed out and boiled with strong soda, the results will be too high, owing to the sulphocyanides"—taken in connection with the preceding paragraph, where milk of lime is prescribed as the proper way of treating the liquor. But a simple experiment shows that milk of lime equally expels the ammonia from ammonium sulphocyanide.

PROPERTIES OF AMMONIA AND ITS TECHNICALLY IMPORTANT SALTS.

Ammonia, NH_3.

Physical Properties.—Colourless gas, of pungent smell and sharp alkaline taste. Common ammonia, owing to its admixture of organic bases (pyridine, etc.), has a much more disagreeable smell than pure. Sp. gr. 0·5967; 1 litre at 0° and 0·76 metre pressure, according to the most exact determinations of Guye and Picoza (1908) weighs 0·7708 g. Perman and Davies (*Proc. Roy. Soc.*, 17th May 1906) found practically the same value, viz., 0·77085. Coefficient of expansion between 0° and 20° = 0·003914, between 0° and 100° = 0·003487. Vapour-tension (according to Bunsen, *Pogg. Ann.*, xlvi., p. 95):—

At − 33°·7 = 1 atmosphere.
" − 5° = 4 atmospheres.
" 0° = 4·8 "
" + 10° = 6·5 "
" + 20° = 8·8 "

Specific heat of gaseous ammonia 0·5009 at 0°, 0·5317 at 100°, and 0·5029 at 200°. The heat of formation of ammonia from the elements is, according to Thomsen = 11890 cal. Haber and Le Rossignol (*Berl. Ber.*, xl., p. 2144) found it for temperatures from 700° to 1000° = 12,000 to 12,800 cal. Nernst (*Z. Elektrochem.*, 1910, p. 100) gives it for various temperatures as follows (for NH_3):—

20°.	800°.	700°.	850°.	1000°.
12,700	13,435	14,915	15,110	14,950 calories.

The same author gives for the molecular heat of ammonia the equation:

$$C_p = 8.62 + 0.0020t + 7.2 \frac{t^3}{10^3}.$$

Numerous papers on the properties of ammonia have been published by Haber in the *Z. Elektrochem.*, 1914 and 1915.

Anhydrous Liquid Ammonia.

Dry gaseous ammonia liquefies at 0° and a pressure of 4·19 atmospheres, or at ordinary pressures at −40° to −50°, forming a colourless, very mobile liquid of strong, light-refractive power, whose physical constants have been found by Dewar as follows:—

Critical temperature . . .	+ 130°
Critical pressure . . .	115 atmospheres
Normal boiling-point . . .	− 33°·7
Fusing point . . .	− 75°

The *boiling-point* of liquid ammonia is stated differently by different authors, principally owing to an under-cooling of the remaining liquid portion by the evaporation. Bunsen found the following values at different pressures:—

1 atmosphere	−36°·8
2 atmospheres	−25°·0
3 „	−14°·5
4 „	− 5°·0
5 „	+ 1°·5
6 „	+ 6°·5

Regnault states the boiling-point at 760 mm. pressure = −38°·5; Loir and Dryon = −35°·7, Lange = −33°·7; Dewar *vide supra*; Gibbs = −33°·46, which is confirmed by E. C. Franklin (*Ann. Phys.* [4], xxiv., p. 367).

If a current of air is passed through liquid ammonia, it evaporates rapidly, and temperature goes down to −80°, part of the liquid solidifying into white, transparent crystals, fusing at −75°·5, of higher specific gravity than that of the liquid ammonia.

The *heat of evaporation* for one g. mol. NH_3 was found by Regnault and Forcrand about 5000 cal. at 15°; at the boiling-point = 5600 to 5730. Hence ammonia has a greater evaporating-heat than all liquids, except water, which explains its extensive use for cold-producing machines. The *melting-heat* of ammonia, according to Massol, is = 1838 cal. (water = 1440 cal.).

The *vapour tension* of ammonia, according to Regnault, is as follows (in mm. of mercury):—

Temperature.	Vapour tension.	Temperature.	Vapour tension.
°C.	mm.	°C.	mm.
−30	866·09	+40	11595·30
−20	1392·13	+50	15158·33
−10	2144·62	+60	19482·10
0	3183·34	+70	24675·55
+10	4575·03	+80	30483·09
+20	6387·78	+90	38109·22
+30	8700·97	+100	46608·24

The following table by A. Lange (*Chem. Ind.*, 1898, p. 91), stating the *specific gravity of anhydrous liquid ammonia at various temperatures*, is of importance, since this substance is a commercial article and its volume varies considerably with the temperature:—

°C.	Specific gravity.	Relative volume, $V_0=1$.	°C.	Specific gravity.	Relative volume, $V_0=1$.	°C.	Specific gravity.	Relative volume, $V_0=1$.
−50	0·6954	0·9119	5	0·6275	1·0105	60	0·5404	1·1735
−45	0·6895	0·9197	10	0·6207	1·0215	65	0·5310	1·1942
−40	0·6835	0·9277	15	0·6138	1·0330	70	0·5213	1·2162
−35	0·6775	0·9359	20	0·6067	1·0451	75	0·5111	1·2407
−30	0·6715	0·9443	25	0·5993	1·0579	80	0·5004	1·2673
−25	0·6654	0·9529	30	0·5918	1·0715	85	0·4892	1·2963
−20	0·6593	0·9617	35	0·5839	1·0860	90	0·4774	1·3281
−15	0·6532	0·9708	40	0·5756	1·1015	95	0·4652	1·3631
−10	0·6469	0·9802	45	0·5671	1·1180	100	0·4522	1·4021
−5	0·6405	0·9899	50	0·5584	1·1355			
0	0·6341	1·0000	55	0·5495	1·1540			

Ellean and Ennis (*J. Franklin Inst.*, 1898, pp. 145, 189, 280) found the *specific heat* of liquid ammonia = 1·0206 at 10° C. For other temperatures the formula 0·9834 + 0·00365 *t* must be used.

The following table (from Erdmann's *Anorg. Chem.*, 1906, p. 212) is of great importance for the manufacture of ice, as it shows the dependence of the *degree of cold produced by the evaporation of liquid ammonia* from the temperature:—

Temperature, °C.	Pressure, grams per sq. c.c.	The gas occupies per gram c.c.	Calories taken up by evaporation, per gram.	Absolute temperature, °C.
−40	720	1607	332·7	233
−30	1190	998	330·6	243
−20	1900	646	327·2	253
−10	2920	432	322·3	263
0	4350	298	316·1	273
+10	6270	211	308·6	283
+20	8790	154	299·9	293
+30	12010	114	289·7	303
+40	16010	87	278·0	313

Liquid ammonia is a bad conductor for *electricity*. An addition of water strongly increases its conductivity. Sometimes the liquid assumes a blue colour on passing the current through it; according to Cady (*J. Phys. Chem.*, i., 707) this is caused by a slight content of alkaline salts which cause the formation of alkali-ammonium (*vide infra*).

Liquid ammonia in many cases behaves like water, forming molecular compounds which behave like the hydrates. It has a strong *solvent power* for many inorganic and organic substances, and, like water, it ionizes the dissolved substances; the conductivity of such solutions of salts is frequently greater than that of their aqueous solutions (Cady, *loc. cit.*). The dissolving power of ammonia has been specially treated by J. Bronn, in his book, *Verflüssigtes Ammoniak als Lösungsmittel* (Berlin, Julius Springer, 1905). *Cf.* also *Amer. Chem. J.*, 1899, pp. 8 *et seq.* It dissolves sulphur, phosphorus, selenium, rubidium, caesium, lithium, potassium, sodium, the two last-mentioned with formation of metal-ammonium compounds. Of inorganic salts it does not dissolve the fluorides, but the alkaline chlorides, bromides and iodides, cyanides, cyanates, thiothianates, nitrites and nitrates. Sulphates are little or not at all soluble.

Very interesting are the *metal-ammonium compounds*, especially those of the alkali metals, which are also formed from gaseous ammonia and alkali metals under high pressure, probably after previous liquefaction of the ammonia. Moissan (*Comptes rend.*, cxxvii., p. 685) has studied them in detail. Gaseous ammonia acts, with liquefaction, with lithium at 70°, with calcium at +20°, with potassium at −2°, with sodium at −20°. From a solution of one atom of sodium in 20 mols. of liquid ammonia, on removing the ammonia dark red sodium-ammonia is separated, which at ordinary temperatures dissociates into sodium amide and water. The ammonium-metals have highly reactive powers, and act on metals with formation of other ammonium compounds. Such are, *e.g.*, Na_3AsNH_3; $K_2As_4NH_3$; $NaPb_4(2NH_3)$.

In concentrated sulphuric acid, according to Loir and Dryon (*Bull. Soc. Chim.*, 1860, p. 184), liquid ammonia is not soluble at low temperatures, and combines with it only quite gradually.

Among organic compounds, those of the methane series are little or not at all soluble in liquid ammonia; easily soluble are benzene and toluene, much less so naphthalene, anthracene, phenanthrene, etc. Easily soluble are aliphatic halogen compounds, alcohols, ether, aldehydes, and esters, nitrogen compounds, oxygen acids, and sugar; little soluble are aromatic halogen and nitrogen compounds. Easily soluble are aromatic amides, phenols, aldehydes and acids, esters, sulpho-acids, acid amides, and anilides; pyridine and quinoline are miscible with it in every proportion, but terpenes are insoluble (Franklin and Kraus, *Amer. Chem. J.*, xx., pp. 820, 836; Spiegel, *Der Stickstoff*, p. 395).

Behaviour of Gaseous Ammonia to Water.—Gaseous ammonia is absorbed by water with great avidity, and with strong development of heat; temperature and pressure playing a very important part. If gaseous ammonia is brought into contact with ice, the latter absorbs it and fuses, the heat produced thereby being stated from 8435 to 8820 cal. by various authors.

The *dissolving-heat* of ammonia (which is very important for the industry of low temperatures) has been found as follows by Hilde Mollier (*Z. Verein. deutsch. Ingen.*, 1909, p. 424).

Percentage of NH_3 of the solution in which the NH_3 is dissolved.	Heat of solution of 1 kg. NH_3.	
	Liquid, 18°.	Gaseous, 15° and 1 atm., calculated with dissolving heat of liquid ammonia.
0	193	493
5	183	483
10	171	471
15	158	458
20	144	444
25	129	429
30	113	413
35	97	397
40	79	379
45	59	359
50	39	339
55	19	319

Steam of 100°, according to Playfair and Wanklyn (*Chem. Soc. Quart. J.*, xv., p. 242), mixes with gaseous ammonia without contraction, which proves that no hydrate of ammonia exists at that temperature. *Water*, according to Roscoe and Dittmar (*Ann. Chem. Pharm.*, cxii., p. 349), absorbs at 760 mm. pressure, and temperatures from 0° to 56° per gram, the following quantities of NH_3:—

t.	Gram NH_3.	*t.*	Gram NH_3.	*t.*	Gram NH_3.	*t.*	Gram NH_3.
0°	0·875	16°	0·582	30°	0·403	44°	0·275
2°	0·833	18°	0·554	32°	0·382	46°	0·259
4°	0·792	20°	0·526	34°	0·362	48°	0·244
6°	0·751	22°	0·499	36°	0·343	50°	0·229
8°	0·713	24°	0·474	38°	0·324	52°	0·214
10°	0·679	26°	0·449	40°	0·307	54°	0·200
12°	0·645	28°	0·426	42°	0·290	56°	0·186
14°	0·612						

The same authors give the grams NH_3 (G) absorbed by 1 g. water, for various partial pressures of the dry gas (P) expressed in metres of mercury:—

P.	G.	P.	G.	P.	G.	P.	G.
0·00	0·000	0·3	0·515	0·9	0·968	1·5	1·526
0·05	0·175	0·4	0·607	1·0	1·037	1·6	1·645
0·10	0·275	0·5	0·690	1·1	1·117	1·7	1·770
0·15	0·351	0·6	0·768	1·2	1·208	1·8	1·906
0·20	0·411	0·7	0·840	1·3	1·310	1·9	2·046
0·25	0·465	0·8	0·906	1·4	1·415	2·0	2·195

Specific Gravities of Aqueous Solutions of Ammonia.

The former tables of the specific gravities of liquor ammoniæ have been superseded by that of Lunge and Wiernik (*Z. angew. Chem.*, 1889, p. 181), which is here subjoined.[1] It refers to a temperature of 15° C.

Spec. grav. at 15° C.	Per cent. NH_3.	1 litre contains grms. NH_3 at 15°.	Correction of spec. grav. for ±1° C.	Spec. grav. at 15° C.	Per cent. NH_3.	1 litre contains grms. NH_3 at 15°.	Correction of spec. grav. for ±1° C.
1·000	0·00	0·0	0·00018	0·940	15·63	146·9	0·00039
0·998	0·45	4·5	0·00018	0·938	16·22	152·1	0·00040
0·996	0·91	9·1	0·00019	0·936	16·82	157·4	0·00041
0·994	1·37	13·6	0·00019	0·934	17·42	162·7	0·00041
0·992	1·84	18·2	0·00020	0·932	18·03	168·1	0·00042
0·990	2·31	22·9	0·00020	0·930	18·64	173·4	0·00042
0·988	2·80	27·7	0·00021	0·928	19·25	178·6	0·00043
0·986	3·30	32·5	0·00021	0·926	19·87	184·2	0·00044
0·984	3·80	37·4	0·00022	0·924	20·49	189·3	0·00045
0·982	4·30	42·2	0·00022	0·922	21·12	194·7	0·00046
0·980	4·80	47·0	0·00023	0·920	21·75	200·1	0·00047
0·978	5·30	51·8	0·00023	0·918	22·39	205·6	0·00048
0·976	5·80	56·6	0·00024	0·916	23·03	210·9	0·00049
0·974	6·30	61·4	0·00024	0·914	23·68	216·3	0·00050
0·972	6·80	66·1	0·00025	0·912	24·33	221·9	0·00051
0·970	7·31	70·9	0·00025	0·910	24·99	227·4	0·00052
0·968	7·82	75·7	0·00026	0·908	25·65	232·9	0·00053
0·966	8·33	80·5	0·00026	0·906	26·31	238·3	0·00054
0·964	8·84	85·2	0·00027	0·904	26·98	243·9	0·00055
0·962	9·35	89·9	0·00028	0·902	27·65	249·4	0·00056
0·960	9·91	95·1	0·00029	0·900	28·33	255·0	0·00057
0·958	10·47	100·3	0·00030	0·898	29·01	260·5	0·00058
0·956	11·03	105·4	0·00031	0·896	29·69	266·0	0·00059
0·954	11·60	110·7	0·00032	0·894	30·37	271·5	0·00060
0·952	12·17	115·9	0·00033	0·892	31·05	277·0	0·00060
0·950	12·74	121·0	0·00034	0·890	31·75	282·6	0·00061
0·948	13·31	126·2	0·00035	0·888	32·50	288·6	0·00062
0·946	13·88	131·3	0·00036	0·886	33·25	294·6	0·00063
0·944	14·46	136·5	0·00037	0·884	34·10	301·4	0·00064
0·942	15·04	141·7	0·00038	0·882	34·95	308·3	0·00065

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[1] A new table, by W. C. Ferguson, in *J. Soc. Chem. Ind.*, 1905, p. 787, gives values practically the same as those found by L. and W.

The last of the four columns shows what correction must be made for figures observed at other temperatures than 15° C., in order to reduce them to that standard; but the temperature of observation ought not to be *very much* above or below 15°, since the coefficient of dilatation may differ. If, for instance, at 13° the specific gravity had been found = 0·900, it should be placed lower by 2 × 0·00057, *i.e.* at 0·899, in order to correct it for 15°, which amounts to a difference of ⅓ per cent. NH_3.

Hydrates of Ammonia.—A concentrated aqueous solution of ammonia, on cooling down to −38° to −41°, solidifies, forming flexible, resplendent needles; at −49° it solidifies into a nearly inodorous jelly. Rupert (*J. Amer. Chem. Soc.*, 1909, p. 866; 1910, p. 748) found the freezing-point of a solution containing 49 per cent. NH_3 = −73°, corresponding to the compounds $NH_3 . H_2O$ (= 48·59 per cent. NH_3) and $2NH_3 . H_2O$ (= 65·40 per cent. NH_3). Eutectic points at 32 per cent. = −115°; at 57·5 per cent. = −86°·5; and at 78·5 per cent. = −96°. The hydrate $NH_3 . H_2O$ forms small, colourless crystals; the crystals of the semi-hydrate, $2NH_3 . H_2O$ or $(NH_4)_2O$, are needle-shaped, much larger, and transparent. Smits and Postma (*Chem. Zentr.*, 1910, i., p. 1217) also found the hydrates, $NH_4 . OH$ (fusing at −77°) and $(NH_4)_2O$, fusing at −75°.

J. Thomson and D. Tommasi (*Chem. Zentr.*, xv., p. 418) on the strength of thermo-chemical and physical observations deny the existence of ammonium hydrates.

The *vapour-pressures* of aqueous solutions of ammonia have been examined by E. P. Perman (*Trans. Chem. Soc.*, lxxix. (1901), p. 718; lxxxiii. (1903), p. 1168). The following is a summary of the values found:

Temperature.	Per cent. NH_3.	Partial pressure of NH_3.	Partial pressure of H_2O.
0°	9·15	24·8	5·3
0°	19·62	82·5	3·0
19°·9	10·15	80·6	15·1
19°·9	19·40	215·6	12·3
40°	11·06	218·6	49·1
40°	20·85	576·1	37·8
60°	3·86	136·9	144·1
60°	11·31	475·8	130·4

Hilde Mollier (*Z. Verein. deutsch. Ingen.*, 1908, pp. 131

et seq.) also established the vapour pressures of aqueous solutions of ammonia for various percentages, temperatures, and pressures.

Solubility of Ammonia in Other Liquids.

Ammonia is soluble in *aqueous solutions of salts* without reacting on the dissolved salts, but differently from its solubility in pure water. According to Gans (*Z. anorg. Chem.*, xxv., p. 236), Rothermund (*Z. physik. Chem.*, xxxiii., p. 401), Abegg and Riesenfeld (*ibid.*, xl., p. 84), the difference is mostly proportional to the percentage of dissolved salts; but solutions of ammonium and sodium nitrate dissolve exactly as much ammonia as pure water, and solutions of potassium nitrate even more. According to Konowalow (*J. Russ. Phys. Chem. Soc.*, xxx., p. 367; *Chem. Zentr.*, 1898, ii., p. 659), a solution of silver nitrate dissolves so much more ammonia than pure water as corresponds to the formation of the compound $AgNO_3+2NH_3$.

Caustic potash and soda solutions have the same dissolving power for ammonia, decreasing with their increase in concentration. Raoult (*Comptes rend.*, lxxvii., p. 1078) found that 100 c.c. saturated potash solution at 16° and 760 mm. pressure take up only 1 g. NH_3; 100 c.c. potash solution of 24·25 per cent. KOH absorb 30 g. NH_3.

Ammonia gas is also soluble in ether and in the various alcohols, but less so than in water. Delépine (*J. Pharm. Chim.*, xxv., p. 496) found the solubility of ammonia in *alcohol* of various specific gravities as follows:—

Strength of alcohol (per cent.)		100.	96.	90.	80.	70.	60.	50.
Temp.								
0°	NH_3 per litre	130·5	146·0	173·0	206·5	...	246·0	304·5
	Spec. grav.	0·782	0·783	0·809	0·808	...	0·830	0·835
10°	NH_3 per litre	108·5	120·0	137·5	167·0	...	198·25	227·0
	Spec. grav.	0·787	0·803	0·794	0·800	...	0·831	0·850
20°	NH_3 per litre	75·8	97·5	102·0	119·75	137·5	152·5	182·7
	Spec. grav.	0·791	0·788	0·705	0·821	0·829	0·842	0·869
30°	NH_3 per litre	51·5	74·0	77·0	81·75	100·3	129·5	152·0
	Spec. grav.	0·798	0·791	0·796	0·826	...	0·846	0·883

Ammonia is also copiously soluble in methyl alcohol.

Commercial wood-spirit containing less than 3 per cent. acetone dissolves, at 0°, 40 per cent. of its weight of NH_3.

Pagliani and Ems (Wiedemann's *Ann.*, viii., Beiblatt, p. 18) give tables of the absorption coefficients of ammonia in ethylic, propylic, and isobutylic alcohol.

Absorption of Ammonia by Solid Substances.

Gaseous ammonia is absorbed by very many solid substances, partly with formation of loose chemical compounds or solutions, partly only by surface action.

Freshly heated wood-charcoal, according to Hunter (*J. Chem. Soc.* [2], ix., p. 76, and x., p. 649), absorbs at a pressure of 760 mm. in each volume:

At 0°	5°	10°	15°	20°	25°	80°	85°
170·7	169·6	163·8	157·6	148·6	140·1	131·9	123·0 vols. ammonia.

Its absorbing-capacity for ammonia decreases at the same pressure with the rise of the temperature, but increases at the same temperature with the increase of pressure. At 0° and at various pressures it amounts for each volume of charcoal to:—

Pressure.	Vols.	Pressure.	Vols.
760 mm.	170·7	1486·5 mm.	183·5
1104·3 "	174·3	1795·1 "	188·7
1178·0 "	176·0	2002·6 "	196·7
1269·2 "	178·2	2608·5 "	209·8
1369·5 "	180·8		

Clayey surface soil, and especially peat, has a great absorbing-capacity for gaseous ammonia. Certain metallic chlorides, especially argentic, zinc and calcium chloride, absorb ammonia, forming compounds with it which are split up at higher temperatures. Owing to this, ammonia gas cannot be dried by calcium chloride. Faraday (*Quart. Journ. of Science*, xix., p. 16) utilized this property of argentic chloride for the preparation of liquid ammonia. Ammonium nitrate absorbs ammonia at all temperatures between −15° and +25°, forming a liquid ("Divers' liquid," *Chem. News*, xxvii., p. 37). At 28° part of the ammonia escapes, leaving behind a solid nitrate of the formula: $NH_4 . NO_3 + NH_3$. *Cf.* also Raoult (*Comptes rend.*, lxxvi., p. 1261). The composition of the colourless liquid obtained at −10°, which according to Divers (*loc. cit.*) and Kuriloff (*Z. physik. Chem.*, xxv, p. 107) is a solution of ammonium nitrate in liquid ammonia, is $=NH_4.NO_3+2NH_3$. Troost (*Comptes rend.*, xciv., p. 789) and Raoult (*ibid.*, p. 1117) have proved the existence of the compounds: $2NH_4.NO_3+3NH_3$ and $NH_4.NO_3+3NH_3$.

Chemical Behaviour of Gaseous Ammonia.

Ammonia is composed of 82·39 per cent. N and 17·61 per cent. H. Two vols. of gaseous ammonia are formed from 3 vols. H and 1 vol. of N.

The heat of formation of NH_3 from the elements is discussed by Haber in *Chem. Zeit.*, 1915, p. 24.

Ammonia is *decomposed* into hydrogen and nitrogen by the *electric current.* Prolonged action of electric sparks decomposes NH_3 into N and H, but never quite completely, since ammonia is formed from N and H by the same agency (Buff and A. W. Hofmann, *Annalen*, cxiii., p. 129; Deville, *Comptes rend.*, lx., p. 217; A. W. Hofmann, *Berl. Ber.*, xxiii., p. 3318; Grove, *Annalen*, lxiii., p. 1).

Ammonia is also decomposed by *heat* into its elements, but very slowly, especially when mixed with other gases. The conditions of this decomposition have been studied by several chemists, *e.g.*, Deville and Troost (*Comptes rend*, lvi., p. 891), Thénard (*Gilb. Ann.*, xlvi., p. 267); and more recently by Ramsay and Young (*J. Chem. Soc.*, 1884, xlv., p. 88). We quote their results somewhat in detail, as the manufacture of ammonia and its recovery as a by-product from the coking of coal, from blast-furnaces, etc., is greatly influenced by this instability of ammonia at high temperatures.

The percentages of ammonia decomposed by heat under varying conditions of temperature, material of the vessel, etc., are as follows:—

(1) With a porcelain tube filled with broken pieces of porcelain:

At 500° C.	1·575	per cent. decomposed.
„ 520°	2·53	„ „
„ 600°	18·28	„ „
„ 620°	25·58	„ „
„ 680°	35·01	„ „
„ 690°	47·71	„ „
„ 810° to 830°	69·50	„ „

(2) With an iron tube filled with broken pieces of porcelain:

At 507° to 527° . . . 4·15 per cent. decomposed.
„ 600° (current very fast) . 21·36 „ „
„ 600° (current much slower) . 34·44 „ „
„ 628° . . . . 65·43 „ „
„ 676° to 695° . . . 66·57 „ „
„ 730° . . . . 93·38 „ „
„ 780° . . . . 100·00 „ „

(3) With a plain glass combustion-tube lying in the iron tube:

At 780° . . . . 0·24 per cent. decomposed.

(4) With a glass combustion-tube filled with fragments of broken glass tubing:

At 780° . . . . 1·72 per cent. decomposed.

(5) With a glass tube filled with strips of ignited asbestos cardboard:

At 520° . . . . 2·90 per cent. decomposed.
„ 780° . . . . 100·00 „ „

(6) With a plain iron tube, no oxide of iron present:

At 780° . . . . 100 per cent. decomposed.

(7) With an iron tube partially oxidized, and therefore water formed:

At 780° . . . . 95 per cent. decomposed.

(8) With a glass tube containing several lengths of iron wire:

At 760° . . . . 75 per cent. decomposed.

(9) With a glass tube containing several lengths of copper wire:

At 760° . . . . 20 per cent. decomposed.

(10) With a glass tube filled with copper reduced from the oxide, to give a large surface:

At 780° . . . . 50·2 per cent. decomposed.

The results may be summed up as follows:—(1) Under the most favourable circumstances (with an iron or porcelain tube, or a glass tube containing asbestos) the temperature at which ammonia-gas begins to decompose is a little below 500°. (2) In contact with a glass surface, the temperature at which decomposition begins is much higher. (3) The influence of the time of exposure is very great. (4) The nature of the surface of the containing-vessel exerts an enormous influence on the amount of decomposition. (5) The amount of decomposition is greater when the surface is increased. The decomposition was never absolutely complete, just as Deville had found when decomposing ammonia by the electric spark; probably because N and H recombine to a very slight extent. Such a combination could not be traced by heating a mixture of dry nitrogen and hydrogen; when the gases were moist a trace of ammonia was formed, probably owing to the production of nascent hydrogen from water and red-hot iron.

According to Berthollet (*Gilb. Ann.*, xxx., p. 378), the dissociation of ammonia by heat is promoted by the presence of certain metals, such as platinum, silver, and gold wire, even more so by copper and iron wire; the metals do not thereby undergo a change of weight, but copper and iron turn brittle. According to Than (*Ann. Chem.*, cxxxi., p. 129) the contemporaneous introduction of inert gases protects part of the ammonia from decomposition. White and Melville found that the dissociation of ammonia commences at about 450°; they did not find it influenced by the presence of inert gases, like nitrogen or hydrogen, if the quantity of ammonia passing through remained the same (*J. Amer. Chem. Soc.*, 1905, p. 373). This agrees with the observations of Deville and Troost (*loc. cit.*), and of Perman and Atkinson (*Z. physik. Chem.*, iv., p. 915), who also confirm the statements of Ramsay and Young (*vide supra*).

Woltereck (*Comptes rend.*, 1908, pp. 147, 460) finds that ammonia, if purified in the ordinary way, which still contains traces of water and organic impurities, begins to dissociate at 620°, and at 650° the gases are explosive. Absolutely dry and pure NH_3 even at 620° shows no trace of dissociation.

Investigations on the reaction:

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

have been made by Haber and Van Oordt (*Z. anorg. Chem.*, xliv., p. 341); Haber and Maschke (*Z. Elektrochem.*, 1914, p. 597; 1915, pp. 128 and 191); by Nernst and Jost (*ibid.*, xiii., p. 521); by Davies (*Z. physik. Chem.*, lxiv., p. 657).

Haber and Van Oordt found for pure ammonia the following equilibria:—

Temperature.	Composition of the mixture at equilibrium.		
	Vol. per cent. H_2	Vol per cent. N_2.	Vol. per cent. NH_3.
27°	1·12	0·37	98·51
327°	68·46	22·82	8·72
627°	74·84	24·95	0·21
927°	75·00	25·00	0·024
1020°	75·00	25·00	0·012

By the action of the *light* of a quartz-mercury lamp ammonia is completely decomposed (Coehn and Prigert, *Z. Elektrochem.*, xx., p. 275).

By *radium emanation*, according to Usher (*Proc. Chem. Soc.*, 1910, No. 366, p. 20), ammonia is quickly decomposed at ordinary temperatures; solid NH_3 less quickly at −190°. The decomposition is hardly at all reversible. The maximum effect was the decomposition of 134,300 mol. NH_3 to 1 atom of emanation. The energy required for this action amounts to about 1 per cent. of the energy actually expended for producing the emanation. Wourtzel (*Comptes rend.*, clviii., p. 571; *Chem. Zentr.*, 1914, i., p. 1482) also investigated this reaction.

Combustibility.—In atmospheric air ammonia burns with great difficulty, requiring constant heating. But, according to Berzelius, in an atmosphere of oxygen it burns by itself with a yellowish flame; according to A. W. Hofmann (*Ann. Chem.*, cxv., p. 285), if a current of oxygen is passed through boiling ammoniacal liquor, and the issuing gas is lighted, it burns with a greenish flame. The temperature of this flame under appropriate conditions is very high; according to Rosenfeld (*Ber.*, xiv., p. 2103; xv., p. 161), it causes lime to glow violently and thick platinum wire to fuse. According to Henry (*Ann. Phil.*, xxv., p. 424) mixtures of air and ammonia gas are not explosive, but by the continuous action of electric sparks they are slowly burnt; but Schlumberger and Piotrowski (*J. Gasbeleucht.*, lvii., p. 941; *Chem. Zentr.*, 1914, ii., p. 1421) found that mixtures of 16·5 to 26·8 vol. NH_3 with 83·5 to 93·2 vol. air do explode in vessels of the form chosen by the observers. In the Bunte burette there was no explosion, but gradual combustion. Kraut (*Ann. Chem.*, cxxxvi., p. 69) found that platinum sponge or platinized asbestos glow up in a mixture of ammonia gas with oxygen or air, with formation of nitrous gases and ammonium nitrite. On dry ammonia gas ozone has no action, but on an ammoniacal solution, with formation of nitrous and nitric acid, but not of hydrogen peroxide (Nagy-Ilosvay, *Ber.*, xxvii., p. 3500).

Behaviour of Dry Ammonia towards Various Elements and Oxides.—Ammonia combines with *chlorine* at ordinary temperatures, with formation of nitrogen and ammonium chloride. If an excess of chlorine is passed into a saturated solution of ammonia, the extremely explosive nitrogen chloride is formed. Solutions of *hypobromites* expel from ammonia and its salts the whole of the nitrogen in gaseous form, upon which reaction the well-known azotometric method of Knop for the estimation of nitrogen is founded.

On red-hot *charcoal* ammonia acts, according to Langlois (*Ann. Chim. Phys.* [3], i., p. 111), with formation of hydrogen and ammonium cyanide; the reaction (according to Weltzien, *Ann. Chem.*, cxxxii., p. 224) is:—

$$2NH_3 + C = NH_4.CN + H_2.$$

If at the same time alkali-metals (Delbrück, *J. prakt. Chem.*, xli., p. 161) or their carbonates (Siepermann, Ger. Ps. 38012 and 51562; Beilby, Ger. P. 74554; Pfleger, Ger. P. 89594) are present, alkaline cyanides are formed.

If dry ammonia acts on fused alkali-metals, 1 atom of hydrogen is substituted by 1 atom of metal, with formation of alkali-amide (Beilstein and Geuther, *Ann. Chem.*, cviii., p. 88; Landolt and Baumert, *ibid.*, cxi., p. 1; Deutsche Gold- und Silber-Scheideanstalt, Ger. P. 117623), according to the equation:

$$2NH_3 + 2Na = 2NaNH_2 + H_2.$$

In the presence of carbon, of carbon oxides, or hydrocarbons, according to Drechsel (Deutsche Gold- und Silber-Scheideanstalt, Ger. Ps. 124977, 126241, 148045, 149678; Castner, Ger. P. 90999) metallic dicyanamides or metallic cyanides are formed.

Many metallic oxides are reduced on heating in a current of ammonia gas, either to the metallic state (*e.g.*, Fe_2O_3 to "ferrum reductum"), or to lower degrees of oxidation, with formation of free nitrogen and water. In other cases there is a formation of nitric oxide, NO (*e.g.*, from ammonia and red-hot manganese peroxide), or of nitrogen peroxide, or (in the case of the oxides of titanium, iron, and copper) of metallic nitrides, or (in the case of tungstic acid and mercuric oxide) of compounds of the metal with nitrogen, hydrogen, and oxygen.

Behaviour of Ammonia towards Other Gases and Liquids.—With gaseous *sulphur dioxide* ammonia combines in various proportions. Schumann (*Z. anorg. Chem.*, xxiii., p. 43) obtained the easily decomposable compounds $SO_2.NH_3$ and $SO_2(NH_3)_2$ in the shape of yellow or red crystalline substances. Divers and Ogawa (*Proc. Chem. Soc.*, xvi., p. 38) obtained on passing both gases into ether, free from water and alcohol, the compound: $NH_2.SO_2.NH_4$. Ephraim and Pietrowsky (*Berl. Ber.*, 1911, p. 379) also describe such compounds.

On passing a mixture of ammonia and *carbon disulphide* vapour through a red-hot tube, hydrogen sulphide and sulphocyanide are formed. If those two substances meet in an alcoholic solution, Debus (*Ann. Chem.*, lxxiii., p. 26) observed the formation of ammonium sulphocarbonate and ammonium sulphocyanide.

If dry ammonia meets *carbon dioxide* at ordinary temperatures, ammonium carbamate is formed:

$$2NH_3 + CO_2 = NH_2.CO.ONH_4;$$

at higher temperatures urea and ammonium carbonate are formed:

$$4NH_3 + 2CO_2 = NH_2.CO.NH_2 + NH_4O.CO.ONH_4.$$

Ammonia also combines with *aldehydes*, forming well-characterised and partly technically important compounds. If, *e.g.*, NH_3 is passed into an alcoholic solution of formaldehyde, a precipitate of hexamethylenetetramine (urotropin) is produced in nearly quantitative yield (Duden and Scharff, *Ann. Chem.*, cclxxxviii., p. 218).

Ammonium hydroxide, NH_4O, has, of course, *basic* properties; but this is doubtful for dry ammonia, NH_3. Spiegel (*loc. cit.*) points out that completely dry gaseous ammonia is not taken up by absolutely anhydrous acids, such as sulphuric monohydrate, nor by acid anhydrides, like CO_2, SO_2, P_2O_5, etc.; this also holds good of absolutely anhydrous liquid ammonia which, according to Loir and Dryon (*Bull. Soc. Chim.*, 1860, p. 184) combines only quite gradually with concentrated sulphuric acid. On red litmus and on turmeric paper ammonia causes the well-known colour reactions only for a little time, up to its volatilization.

Physiological Properties.—Ammonia is an irritant and corrosive agent, both in the shape of gas and of aqueous solution. The former researches of Pettenkofer (*Sitz.-Ber. bayer. Akad.*, 1887, p. 179), Hasselt (*Thiergifte und Mineralgifte*, 1862, p. 183), and Eulenburg (*Schädliche und giftige Gase*, 1865, p. 190) have been superseded by those of K. B. Lehmann (*Arch. f. Hygiene*, 1886). One-twentieth volume NH_3 per 1000 impart to air a strong smell; 0·3 to 0·35 per 1000 is the strongest dose bearable for half an hour, but it does not act as a real poison, only as an irritant upon the mucous membranes, which can be borne much better by those accustomed to it. Doses of 2 vols. per 1000 when inhaled for a prolonged time, or doses of 5 vols. per 1000 for a short time, produce a severe and consequently dangerous irritation of the respiratory organs and the mucous membranes of the eye, but only locally, without causing any injury to the other organs or their functions.

The men employed at ammonia-works may contract inflammation of the eyes, stinging headaches, and a peculiar affection of the skin, resulting in eruptions and cracks. The counter-poisons are acetic or tartaric acid, diluted with sugar-water; the former may also be employed for inhalation. Hot baths are recommended for promoting the removal of the ammonia through the skin.

Gottbrecht (*Arch. experim. Pathol.*, xxv., p. 385) found that ammonia also possesses antiseptic properties.

The properties and behaviour of ammonia have been investigated by F. Haber, in conjunction with various co-operators, at the Institute for physical chemistry and electro-chemistry at Berlin-Dahlem; the results are published in *Z. Elektrochem.*, 1914, xx., p. 597; 1915, xxi., pp. 89, 128, 191, 206, 228, 241.

Chemical Behaviour of Aqueous Solutions of Ammonia (liquor ammoniæ).—This behaviour is generally the same as that of anhydrous ammonia; but there are some important exceptions.

to this rule. *Ozone*, e.g., does not oxidize gaseous ammonia, but with aqueous solutions of ammonia it forms large quantities of nitrous and nitric acid. Towards *sulphuric monohydrate* ammonia in aqueous solution behaves like a strong base, whilst dry gaseous NH_3 does not act upon it (*vide supra*).

Behaviour of Ammonia Solutions against Electricity.—Faraday found that concentrated ammonia solutions do not conduct electric currents any better than pure water; but the presence of small quantities of ammonium sulphate increases the rate of decomposition, whereby 1 vol. of nitrogen and 4 vols. of hydrogen are formed, together with small quantities of oxygen. An apparent deficiency in the amount of nitrogen, according to Losanitsch and Jovitschitsch (*Ber.*, xxix., p. 2436) is caused by the formation of nitrite. According to Hisinger and Berzelius (*Gilb. Ann.*, xxxvi., p. 260) concentrated ammonia solutions, with employment of iron electrodes, yield pure nitrogen at the positive pole; ammoniacal liquor, diluted with 3 vols. of water, gives off also oxygen, with formation of ferric oxide.

Sulphur is soluble in ammonia solutions, as observed already in 1752 by Boerhave; at 90° the liquor assumes a yellow colour, with formation of thiosulphate, sulphide, and polysulphides (Brunner, *Dingl. polyt. J.*, cli., p. 371; Flückiger (*Z. anal. Chem.*, ii., p. 398).

Chlorine acts on aqueous ammonia as on the dry gas, with formation of ammonium chloride and nitrogen (A. W. Hofmann, *Ann. Chem.*, cxv., p. 283):

$$4NH_3 + 3Cl = 3NH_4Cl + N.$$

On mixing aqueous solutions of ammonia with hypochlorous acid, there is a formation of nitrogen and explosive nitrogen chloride. Similar compounds are formed with bromine and iodine.

Hydrogen sulphide, when passed into ammonia solutions, forms the hydrosulphide, $H(NH_4)S$, and monosulphide $(NH_4)_2S$, which combine with more sulphur to form polysulphides.

Saturated solutions of ammonia and of *potassium carbonate* are only miscible, if to 1 vol. of potassium carbonate 30 vols. of liquor ammoniæ of sp. gr. 0·88 is added.

Against solutions of the *salts of heavy metals*, liquor ammoniæ generally behaves like the solutions of alkali hydrates. Hence it is frequently assumed that that liquor contains ammonium hydrate, $NH_4.OH$, which seems to be confirmed by the existence of ammonium amalgam, analogous to potassium and sodium amalgam (Coehn, *Z. anorg. Chem.*, xxv., p. 430). Knorr (*Ber.*, xxxii., p. 729) found in ammonia solutions not merely NH_4 – and OH – ions, but also NH_2 – or $NH_3.OH$ – ions. But this view is not confirmed by the thermochemical and physical investigations of Jul. Thomsen (*Chem. Zentr.*, xv., p. 418) and Tommasi (*Comptes rend.*, xcviii., pp. 140, 326, 797), nor by those of Hantzsch and Sebaldt (*Z. physik. Chem.*, xxx., p. 258), according to whom there exists only a loose compound, $NH_3.H_2O$, dissociating already at ordinary temperatures.

Many *metallic salts* combine with aqueous ammonia in definite proportions, forming metal-ammonium compounds, of which especially those of cobalt and of platinum have a high degree of stability.

Aqueous ammonia combines with *anhydrous acids*, forming salts without excretion or absorption of water, *e.g.*,

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

The salts are isomorphous with those of potassium; their solutions are at higher temperatures partially hydrolytically dissociated. Watson Smith, in *J. Soc. Chem. Ind.*, 1911, pp. 253 *et seq.*, enumerates the literature on that subject, and describes experiments of his own thereon. This dissociation is especially pronounced in the case of solutions of ammonium chloride, which explains their destructiveness on iron evaporating-vessels, to be mentioned below; but it takes place to some extent also with ammonium sulphate, nitrate, phosphate, oxalate, acetate, etc.

With *carbon disulphide* a 25 per cent. aqueous solution of ammonia combines on heating under pressure to 110° smoothly to ammonium sulphocyanide:

$$CS_2 + 2NH_3 = NH_4.CNS + H_2S,$$

a reaction formerly used for the synthesis of cyanides (Tscherniak and Günzburg, Ger. Ps. 3199 and 16005).

Ammonia is recommended as a material for working *aerial shipping-vessels*, by A. Sander, in *Chem. Zeit.*, 1915, p. 325.

Ammonium Sulphides.

There exist a monosulphide $(NH_4)_2S$, a sulphhydrate, NH_4SH, and several polysulphides, containing from 3 to 7 atoms of S to 2 mols. of NH_4. They are all volatile, soluble in water, and easily decomposable.

Ammonium Monosulphide $(NH_4)_2S$, is produced from hydrogen sulphide and ammonia in excess. At −18° it forms colourless shining crystals, dissolving readily and without colour in water. This solution is stable, whilst the crystals in the air at once lose half their ammonia. In the state of vapour it cannot exist, but dissociates into NH_3 and H_2S.

Ammonium Sulphhydrate, NH_4SH, is formed by passing hydrogen sulphide into liquor ammoniæ to saturation (the ordinary laboratory reagent). The originally colourless solution soon turns yellow in the air, polysulphides being formed. Below −10° it can be crystallized; on evaporation it dissociates into H_2S and NH_3. On prolonged contact with air the solution deposits sulphur, and ammonium thiosulphate is formed.

The polysulphides are also prepared by dissolving sulphur in ordinary ammonium sulphide.

Ammonium sulphide has not hitherto been manufactured on a large scale; but this might be done, according to Spence, by mixing in a retort sulphate of ammonia with alkali waste or spent gas-lime (both of them very rich in calcium sulphide), blowing in steam, and passing the vapours into a condensing-apparatus. Care must, however, be taken lest the pipes be stopped up by solidifying ammonium sulphide.

Ammonium Sulphocyanide (*Thiocyanate*) $NH_4.CNS$.

Colourless shining scales, without water of crystallization; the salt crystallized from an aqueous solution is somewhat deliquescent; that crystallized from alcohol is stable in the air. Very soluble in water, with considerable lowering of the temperature, and in alcohol. One hundred parts water of 0° dissolve 122 parts, 100 water of 20° 162·2 parts of this salt. On heating the dry salt it fuses at 149°, and decomposes soon after. Consequently it cannot exist in the state of vapour, but is only formed on cooling from ammonium sulphide and carbon disulphide,

$$(NH_4)_2S + CS_2 = NH_4.NCS + 2H_2S,$$

or else from ammonium cyanide and sulphide. In English gas-liquors from 3 to 5 oz. of ammonium sulphocyanide per gallon is found. It is also found in considerable quantities in the spent oxide of iron of the gas-purifiers.

With metallic sulphocyanides, *e.g.* that of mercury, silver, tin, etc., it forms double salts.

Ammonium Cyanide, $NH_4.CN$.

A colourless salt, crystallizing in cubes, smelling and tasting both of prussic acid and ammonia, with an alkaline reaction, as poisonous as prussic acid. It is very soluble in water and alcohol; it is very volatile, boiling, according to some chemists, at 36°; but, judging from its vapour-density, it must be assumed to undergo dissociation into ammonia and prussic acid. The dry salt is very unstable, and in the air is quickly converted into a brown nitrogenous substance (azulmic acid).

Carpenter and Linder (*J. Soc. Chem. Ind.*, 1904, p. 577) estimate the cyanide in ammoniacal liquor by distilling it with an excess of tartaric acid in an apparatus such as serves for ammonia distillation, adding plumbic nitrate and ferrous chloride, and titrate the HCN in the distillate by 1/10 normal silver nitrate or 1/10 normal iodine.

Ammonium cyanide is no article of trade, but it is formed as an intermediate product in the synthesis of cyanides from ammonia and carbon, and in large quantities at the destructive distillation of vinasse, or in the overheating of the gases formed in this operation.

Ammonium Ferrocyanide, $(NH_4)_4,Fe(NC)_6+3H_2O$.

This salt crystallizes in lemon-yellow crystals of the monoclinic system, like potassium ferrocyanide. It is easily soluble in water, insoluble in alcohol. It is not a technical product, but is formed, like the cyanide, as an intermediate product in the production of cyanides from the gases of destructive distillation.

Another ferrocyanide, $(NH_4)_2,Fe_2(NC)_6$, is insoluble in water, and therefore specially adapted for producing cyanide; also the compound, $(NH_4)_6,Fe,[Fe(NC)_6]_2$, observed by Bueb.

They are described in detail in Bertelsmann's *Technologie der Cyanverbindungen*, 1906, pp. 222 *et seq.*

There exist numerous double compounds of the ammonium ferrocyanides, especially with the alkaline nitrates.

Ammonium Chloride (*Sal-ammoniac*), NH_4Cl.

This salt is known from ancient times; it is found ready formed in nature, especially in volcanic districts and in the vicinity of coal-fields. In the pure state it is without colour or taste. Crystallizes from water or alcohol in octahedra arranged in the form of feathers, from urea in cubes. Sublimed sal-ammoniac consists of fritted fibrous crystalline masses. It is very tough and difficult to powder. Sp. gr. 1·52. Soluble in water, with much absorption of heat; 100 parts of water dissolve, according to Mulder, at

0°	10°	20°	30°	40°	50°	60°	
29·7	33·3	37·2	41·4	45·8	50·4	55·2	parts of the salt.
70°	80°	90°	100°	110°	115°		
60·2	65·6	71·3	77·3	83·8	87·3		

115° is the boiling-point of the saturated solution, whose cryohydric point is = −16°.

The solubility decreases with increasing pressure. The solution of sal-ammonia in water causes a considerable increase of volume; according to Thomsen (*Z. physik. Chem.*, xiii., p. 401), 38 c.c. on dissolving 1 gram-mol. NH_4Cl in 30 to 40 gram-mols. of water.

Specific gravity of Aqueous Solutions of Ammonium Chloride at 15° (Gerlach).

Per cent.	Spec. grav.	Per cent.	Spec. grav.	Per cent.	Spec. grav.
1	1·00316	10	1·03081	19	1·05648
2	1·00632	11	1·03370	20	1·05929
3	1·00948	12	1·03658	21	1·06204
4	1·01246	13	1·03947	22	1·06479
5	1·01580	14	1·04325	23	1·06754
6	1·01880	15	1·04524	24	1·07029
7	1·02180	16	1·04804	25	1·07304
8	1·02481	17	1·05086	26	1·07375
9	1·02781	18	1·05367		

It is very little soluble in absolute alcohol (0·62 per cent.);

of course much more in alcohol containing water. Absolute methylic alcohol dissolves 3·52 per cent. It is easily soluble in liquid ammonia (Franklin and Kraus, *Amer. Chem. J.*, 1898, xxviii., p. 820). From its saturated aqueous solution it is partly precipitated by concentrated hydrochloric acid.

Ammonium chloride forms crystallized double salts with many metallic chlorides, *e.g.*, those of mercury, silver, copper, platinum, gold, etc.

Neutralizing-heat of NH_3 and Cl in aqueous solution = 12·27 cal. (Thomsen).

Ammonium chloride is not volatile at the ordinary temperature, but is considerably so at the temperature of boiling water. According to K. Kraut (*Z. anorg. Chem.*, v., p. 278), on heating it on the water-bath, 48·9 per cent. volatilize in 269 hours. On being heated further, it evaporates without fusing and sublimes in crusts (as above mentioned). Its vapour is a dissociated mixture of NH_3 and HCl. Al. Smith (*Z. Elektrochem.*, 1916, p. 34) gives a table of the vapour-pressures of ammonium chloride from 280° to 330°, and the degree of dissociation calculated therefrom.

Action on Metals.—On boiling its aqueous solution a little ammonia escapes, and the reaction becomes distinctly acid; hence it strongly acts upon metallic (especially iron) vessels, and is thereby contaminated. Even in the neutral state ammonium chloride in the presence of water acts strongly upon iron, copper, etc., and promotes the corrosion of these metals. On the behaviour of solutions of ammonium chloride towards metals, Santi (*Chem. Zentr.*, 1904, p. 1625) has made an extensive investigation. Iron and magnesium are quickly acted upon, with liberation of hydrogen and ammonia, and formation of double salts: $FeCl_2(NH_4Cl)_2$, and $MgCl_2(NH_4Cl)_2$; cadmium, zinc, chromium, manganese are also dissolved more or less.

On heating *metallic oxides* with dry sal-ammoniac they are transformed into chlorides, excepting nickel and cobalt oxides which are reduced to the metallic state. On boiling a solution of ammonium chloride with the protoxides of nickel, iron or manganese, these are transformed into the chlorides (like the carbonates of Ca, Mg, Cu, Co, and Ni), whilst the sesquioxides of No, Fe, and Mn are not acted upon. The *sulphides* of tin and antimony are decomposed by ammonium chloride at higher temperatures; those of manganese and (less easily) of zinc act on a solution of ammonium chlorides. *Thiosulphates*, on boiling with a solution of ammonium chloride, are decomposed according to the equation:

$$Na_2S_2O_3 + 2NH_4Cl = 2NaCl + 2NH_3 + H_2O + SO_2 + S.$$

Manganates are already in the cold transformed by it into permanganates; *chromates* into bichromates and ultimately into chromic acid.

The reaction of ammonium chloride with *barium peroxide* furnishes oxygen, in a practicable way for laboratory use:

$$BaO_2 + 2NH_4Cl = BaCl_2 + 2NH_3 + H_2O + O.$$

Potassium persulphate on boiling with a solution of NH_4Cl gives off chlorine and nitrogen; the residual solution contains hypochlorite.

Ammonium bromide and iodide have no technical importance.

Ammonium Fluoride.

We know a neutral and an acid fluoride. The *neutral* salt, NH_4F, forms hexagonal prisms of strong, salty taste, deliquescent in damp air. It is not much soluble in alcohol, but in water; on heating that solution, ammonia is given off and the acid salt is formed. The solution decomposes silicates, with formation of ammonium silicofluoride.

The *acid* salt, NH_4F,HF, crystallizes in colourless rhombic prisms, easily soluble in water and deliquescent in damp air.

Ammonium fluoride forms with the fluorides of antimony and chromium double fluorides, not decomposed by water, which are employed in dyeing, *e.g.*, as surrogate for tartar emetic. The simple salt is employed for etching glass. Schönfeld (*Wochenschrift für Brauerei*, 1901, p. 297) recommends a 4 per cent. aqueous solution for cleaning and sterilizing the tubes of beer-pression apparatus.

According to Mills (Grossmann, *Das Ammoniak*, p. 87), ammonium fluoride is manufactured by subliming an intimate mixture of finely ground calcium fluoride and ammonium sulphate from an iron pot, lined with plaster of Paris, with a water-cooled cover, on which the fluoride collects when heating the pot above 350°.

Ammonium Carbonates.[1]

Several of the compounds of carbonic acid and ammonia formerly assumed to exist are not acknowledged now, and only those mentioned below are recognized. They are all decomposed at 58° to 60° into carbon dioxide, ammonia, and water; hence they do not exist as compounds in the gas while hot, but are only formed on its cooling. According to Hertkorn (*Chem. Zeit.*, 1891, p. 1493), carbon dioxide with aqueous ammonia forms first carbamate, which is converted into carbonate only on boiling.

Neutral salt $(NH_4)_2CO_3,H_2O$ (first described by Divers).—Lengthened plates; smells and tastes like ammonia; deliquesces in the air with formation of acid salt, losing ammonia and water; splits up at 58° into water, carbon dioxide, and ammonia. When it is dissolved in water, it can be recrystallized, and is not changed by cooling; but the dilute aqueous solution, according to some, already contains a mixture of free ammonia and neutral and acid ammonium carbonate. (This statement is denied by Divers.) The aqueous solution begins to give off gas at 70° or 75°, boils at 75° or 80°, and gives off CO_2 and NH_3 in proportion as they exist in the salt. Heat of formation at 7° to 11° = 39·3 cals.

Semiacid salt $(NH_4)_4H_2(CO_3)_3,H_2O$.—Thin hexagonal plates; smell and taste of ammonia. Decomposed by a little water; dissolves unchanged in 5 parts of water at 15°, which solution rapidly evolves gas when heated (Divers).

Acid salt $(NH_4)H(CO_3)$ = ammonium bicarbonate, is found ready formed in many guano-beds, etc., also frequently in gas-purifiers, pipes, etc. This salt is usually assumed to exist in gas-liquor; but some assert that the other carbonates occur there as well. Some of the commercial carbonate of ammonia manufactured in England is nothing but the bicarbonate, as proved by the analyses of Hanekop (*Arch. Pharm.*, 1886, xxiv., p. 21) and Reissmann (*Pharm. Centralhalle*, 1886, p. 105)

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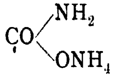
[1] An extensive memoir on the combinations of carbonic anhydride with ammonia and water has been published by E. Divers (*J. Chem. Soc.*, 1870, vol. viii., p. 171). The following statements are to a great extent based on that memoir, and are supplemented by private communications, kindly made to the author by Dr Divers, which partly rectify the extracts from Gmelin-Kraut's *Handbook*, given in the first edition of this work.

It is always formed when the other salts richer in ammonia or ammonium carbamate effloresce. According to Divers, the condition for its formation seems to be the introduction of aqueous vapour and ammonia in atomic proportions into carbonic anhydride, so slowly that the water is never in sufficient quantity to condense to the liquid state; a warm condenser, therefore, is favourable to it. It forms a white mealy powder or rhombic crystals, mostly columnar. Sp. gr. 1·573 (Schiff); the natural salt = 1·45 (Ulex). In the dry state it does not smell of ammonia; it has a cooling and saline taste. In dry air it is stable; in moist air the crystals lose their brilliancy, decomposition setting in (Berthelot and André, *Bull. Soc. Chim.*, xlvii., p. 848). At 60° it slowly decomposes into CO_2,NH_3, and H_2O. It readily dissolves in water; in the air the solution rapidly loses carbonic acid, and on being gently heated gives off gas-bubbles, a salt richer in ammonia remaining behind. According to Dibbits (*Dingl. polyt. J.*, ccxvi., p. 164), 100 parts of water dissolve

At 0°	10°	15°	20°	25°	30°	
11·9	15·8	18·3	21·0	23·9	27·0	parts of salt.

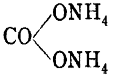
On dissolving a gram-mol. in 25 water of 15°, 6·9 cals. are absorbed (Berthelot and André).

Ammonium carbamate (formerly called dry ammonium carbonate),



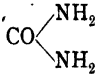
$$CO\begin{cases}NH_2\\ONH_4\end{cases}$$

is the intermediate term between neutral ammonium carbonate,



$$CO\begin{cases}ONH_4\\ONH_4\end{cases}$$

and carbamide or urea,



$$CO\begin{cases}NH_2\\NH_2\end{cases}$$

It is always formed when ammonia and carbon dioxide meet nearly in the dry state and not too hot, and even in the presence of moisture, if at least 2 vols. NH_3 are present to 1 vol. CO_2; hence it is a principal component of commercial ammonium carbonate, and can be obtained from this by slow distillation, etc. It occurs in prisms or crystalline laminæ or crystalline crusts, smells strongly of ammonia, deliquesces in the air, and almost completely volatilizes.

The vapour-tensions of ammonium carbamate are (in millimetres) (Naumann, *Ber.*, 1871, p. 783; Erckmann, *ibid.*, 1885, p. 1157):—

At 0°, 12·4	At 30°, 124	At 54°·75, 563
„ 10°, 29·8	„ 40°, 248	„ 56°·5, 632
„ 20°, 62·4	„ 47°·25, 361	

The vapours consist of a mixture of NH_3 and CO_2.

At 59° to 60° it decomposes entirely into CO_2 and $2NH_3$; at 50° to 55° it is reformed from these components. It dissolves in 1½ parts of water with considerable absorption of heat, and is then quickly converted into the acid salts, ammonia being given off.

Commercial carbonate of ammonia, salt of hartshorn, sal volatile, is a mixture of ammonium bicarbonate and ammonium carbamate, usually containing a little adhering water. It is formed on cooling a mixture of carbon dioxide (even in excess) and ammonia-gas in the presence of sufficient aqueous vapour. According to the opinion once generally entertained, it is also formed in the quick distillation of any of the ammonium carbonates, or of ammonium chloride or sulphate with chalk; but Divers has proved that in this case the neutral carbonate is formed, and this is only converted into the "commercial" carbonate in the process of redistillation (sublimation). Experiments made in my own laboratory have entirely confirmed this observation. In all these cases no doubt carbon dioxide, ammonia, and water must be assumed to exist free while in the state of vapour. Formerly the commercial salt was generally composed according to the formula:

$$2(NH_4)HCO_3,\ CO(NH_2)(ONH_4),$$
$$= 28{\cdot}81\ NH_3,\ 55{\cdot}96\ CO_2,\ 15{\cdot}25\ H_2O;$$

when gently heated in a retort it gradually liquefied, and dissolved

At 18°	16°·7	82°	40°·6	49°
in 4	3·3	2·7	2·4	2 parts of water.

Divers has proved that the salt analyzed by him (in 1870) was richer in ammonia, corresponding to the formula:

$$(NH_4)HCO_3,\ CO(NH_2)(ONH_4),$$
$$= 32{\cdot}48\ NH_3,\ 56{\cdot}05\ CO_2,\ \text{and}\ 11{\cdot}47\ H_2O.$$

It remains solid on heating; in the air it effloresces, losing 47 per cent. by weight, and leaving friable ammonium bicarbonate behind (of which the commercial salt now sometimes consists altogether, *cf.* p. 1315). The same is left when the salt is treated with a small quantity of water.

Vogler (*Z. anal. Chem.*, xvii., p. 451) also considers commercial carbonate of ammonia to be a compound of acid ammonium carbonate with ammonium carbamate. His observations differ from those of Divers only by a direct estimation of the combined water.

According to information received from one of the largest German ammonia manufacturers, two qualities of carbonate of ammonia are found in commerce, one containing about 30 per cent. NH_3 (approaching Divers's formula) and the other containing about 25 per cent. NH_3. Their value as baking powders is nearly the same. The acid carbonate (with 21·5 per cent. NH_3) is only occasionally made.

Commercial "household ammonia," according to Snell (*J. Soc. Chem. Ind.*, 1914, p. 1177), in the *liquid* form shows from 1·64 to 10·92 g. NH_3 in 100 c.c. Four samples of *solid* household ammonia contained the following percentages: water 16·05 to 18·39; ammonium carbamate (containing 30 per cent. NH_3) 1·97 to 9·63; sodium carbonate 57·50 to 78·14; sodium sulphate 3·00 to 13·56; sodium chloride 0·45 to 0·89.

Solutions of Carbonate of Ammonia.—Commercial carbonate of ammonia dissolves at 15° in 4 parts of water, with considerable absorption of heat, at 65° in 1½ parts. At 75° the solution begins to give off much CO_2, at 85° also ammonia; at 100° all the salt is volatilized. In dilute solutions the liberation of the salt takes place later on (Divers).

The specific gravity of the solutions of commercial ammonium carbonate has been determined by J. H. Smith, with my cooperation (*J. Soc. Chem. Ind.*, 1883, p. 80). The salt experimented on had the composition: 31·3 per cent. NH_3, 56·6 per cent. CO_2, 12·1 per cent. H_2O, which most nearly approaches Divers's formula. The table given below shows the specific gravities of the solutions at 15° and the factor for reducing the specific gravities, found at other temperatures, to 15°.

Suppose we have found a specific gravity of 1·108 at 19°, we shall find that at $15^\circ = 1{\cdot}108 + 0{\cdot}0007\ (19 - 15) = 1{\cdot}1108 = 33{\cdot}71$ per cent. ammonium carbonate.

Degrees Twaddell.	Spec. grav. at 15°.	Per cent. ammon. carbonate.	Spec. grav. Factor for 1° C.	Degrees Twaddell.	Spec. grav. at 15°.	Per cent. ammon. carbonate.	Spec. grav. Factor for 1° C.
1	1·005	1·66	0·0002	16	1·080	23·78	0·0006
2	1·010	3·18	0·0002	17	1·085	25·31	0·0006
3	1·015	4·60	0·0003	18	1·090	26·82	0·0007
4	1·020	6·04	0·0003	19	1·095	28·33	0·0007
5	1·025	7·49	0·0003	20	1·100	29·93	0·0007
6	1·030	8·93	0·0004	21	1·105	31·77	0·0007
7	1·035	10·35	0·0004	22	1·110	33·45	0·0007
8	1·040	11·86	0·0004	23	1·115	35·08	0·0007
9	1·045	13·36	0·0005	24	1·120	36·88	0·0007
10	1·050	14·83	0·0005	25	1·125	38·71	0·0007
11	1·055	16·16	0·0005	26	1·130	40·34	0·0007
12	1·060	17·70	0·0005	27	1·135	42·20	0·0007
13	1·065	19·18	0·0005	28	1·140	44·29	0·0007
14	1·070	20·70	0·0005		1·1414	44·90	0·0007
15	1·075	22·25	0·0006				

AMMONIUM SULPHATES.

Several sulphates of ammonia are known: the neutral salt, $(NH_4)_2SO_4$, the acid salt, $NH_4.H.SO_4$, a basic sulphate, $(NH_4)_3.HSO_4$, the pyrosulphate $(NH_4)_2S_2O_7$, and an octosulphate, $(NH_4)_2O.(SO_4)_8$. The only one of these which possesses technical importance is the *neutral* salt $(NH_4)_2SO_4$, which forms transparent rhombic crystals, isomorphous with potassium sulphate. The ammonium sulphate found in the volcanic regions of South Italy is called *mascagnine.* Sp. gr. 1·76; bitter, acrid taste. It decrepitates on heating. The statement found in the text-books that it fuses at 140°, rests according to Watson Smith (*J. Soc. Chem. Ind.*, 1895, p. 629; 1896, p. 3; 1911, p. 253) on a misunderstanding of a remark made by Marchand. Normal ammonium sulphate has *no* fusing-point; when heated it decomposes before fusion into free ammonia and the acid salt, $NH_4.HSO_4$, which then fuses at 140°, as confirmed by Reik (*Monatsh.*, 1902, p. 1033). It behaves just in the same way under diminished pressure, and *in vacuo*, and cannot be sublimated. The acid sulphate fuses, but does not distil, even on heating over the Bunsen burner up to a dark red heat.

One hundred parts of water dissolve at

0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
71·0	73·65	76·3	78·95	81·6	84·25	86·9	89·55	92·2	93·85	97·5

parts of the neutral salt. The saturated solution contains 115·3 parts to 100 parts water, and boils at 108°.

Specific gravity of the Solutions of Ammonium Sulphate at 15° C.

Per cent.	Spec. grav.	Per cent.	Spec. grav.	Per cent.	Spec. grav.
1	1·0057	18	1·1035	35	1·2004
2	1·0112	19	1·1092	36	1·2060
3	1·0172	20	1·1149	37	1·2116
4	1·0230	21	1·1207	38	1·2172
5	1·0287	22	1·1265	39	1·2228
6	1·0345	23	1·1323	40	1·2284
7	1·0403	24	1·1381	41	1·2343
8	1·0460	25	1·1439	42	1·2402
9	1·0518	26	1·1496	43	1·2462
10	1·0575	27	1·1554	44	1·2522
11	1·0632	28	1·1612	45	1·2583
12	1·0690	29	1·1670	46	1·2644
13	1·0747	30	1·1724	47	1·2705
14	1·0805	31	1·1780	48	1·2766
15	1·0862	32	1·1836	49	1·2828
16	1·0920	33	1·1892	50	1·2890
17	1·0977	34	1·1948		

Ammonium sulphate is insoluble in strong alcohol; but soluble in 500 parts alcohol sp. gr. 0·872, or in 62·5 parts alcohol sp. gr. 0·90. It dissolves easily in strong or weak liquor ammoniæ. In these solutions the sulphates of potassium and ammonium replace each other, so that on the addition of one of the solid salts to the solution a corresponding part of the dissolved salt is precipitated. The aqueous solution, according to Gladstone (*Jahresber.*, 1859, p. 118), on evaporation loses part of the ammonia; if evaporated in presence of hydrochloric acid, ammonium chloride and acid sulphate are formed. The solution in water causes a depression of temperature, amounting to 2·4 cals. on dissolving 1 mol. in 400 mols. water. The heat evolved in neutralizing 1 gram-mol. NH_3 in H_2SO_4, both in solutions, is 28·2 to 29 cals.

The *black colour* sometimes occurring in commercial sulphate of ammonia, according to J. van den Bossche (*J. Gas Lighting*, 1914, cxxvi., p. 103) is caused by the presence of iron in the sulphuric acid employed for its manufacture.

Ammonium Sulphites.

A normal, $(NH_4)_2SO_3$, and an acid sulphite, $NH_4.H.SO_3$, are known, neither of which is an article of commerce; but they form an intermediate stage in some processes of the manufacture of sulphate, into which they pass on exposure to the air.

The normal salt crystallizes in monoclinic, deliquescent plates, the acid salt in rhombic prisms. On prolonged exposure to the air they take up oxygen and pass over into sulphates, giving out heat.

According to Deck (B. P. 17050, of 1887) the sulphite acts better than the sulphate as a fertilizer. It plays an important part in the gas-purifying process of Burkheiser (p. 1199), by which the sulphuretted hydrogen is converted into sulphur dioxide, which is employed for taking out the ammonia.

Ammonium Thiosulphate, $(NH_4)_2S_2O_3$.

This salt is formed on the oxidation of ammonium sulphide and is technically obtained from the calcium salt by double decomposition with ammonium carbonate. It crystallizes in tabular or prismatic monoclinic crystals, deliquescent in the air. According to Spring (*Berl. Ber.*, vii., p. 1157) it can be sublimated without decomposition; but Divers and O'Haga (*J. Chem. Soc.*, lxxvii., p. 335) found that it decomposes already at 150° almost completely, leaving behind sulphur, whilst ammonium sulphate sublimates and NH_3 and H_2S go away. It is applied to some extent in photography.

Ammonium Persulphate, $S_2O_8(NH_4)_2$.

This salt, which has found some application as an oxidizing agent, is produced by electrolyzing a solution of ammonium sulphate in sulphuric acid. It forms easily soluble monoclinic prisms. Heat of neutralization for ½ mol. = 12·4 cals.; heat of solution of 1 part in 125 parts of water = −9·7 cals.

Under the influence of many agencies it yields up oxygen, with liberation of heat:

$$(NH_4)_2S_2O_8, 400 \text{ aq.} + H_2O$$
$$= H_2SO_4 \text{ aq.} + (NH_4)_2SO_4, \text{ aq.}, + O + 37.1 \text{ cals.}$$

Ammonium Nitrite, $NH_4 . NO_2$.

This salt is found in the air after violent electric discharges. It is obtained by double decomposition of plumbic nitrite and ammonium sulphate as a crystalline, elastic, tough mass, deliquescent in the air.

According to Traube and Biltz (*Berl. Ber.*, 1904, p. 3110) it is obtained by the action of electrolytic oxygen on ammonia in the presence of copper hydroxide as catalyser, with very good yield.

The dry salt is decomposed on being slowly heated. The solution, on standing or slow heating, is smoothly decomposed into nitrogen and water:

$$NH_4 . NO_2 \rightarrow 2H_2O + N_2.$$

When quickly heated to 60° to 70° or by a blow the salt detonates with explosive violence. Its decomposition by slow heating is utilized in the manufacture of india-rubber balls by the process of E. Herbst.

Ammonium Nitrate.

This salt has already been prepared by Glauber and described as *nitrum flammans.* It is obtained by slow evaporation of the aqueous solution in rhombic prisms, or by rapid boiling as a fibrous mass. Sp. gr. 1·64 to 1·79. Neutralizing-heat of NH_3 and HNO_3 in dilute solutions = 12·3 to 12·5 cals. On heating, it melts at 166°, and on further heating, it is smoothly decomposed into water and nitrogen protoxide:

$$NH_4NO_3 = 2H_2O + N_2O.$$

This property is utilized for the manufacture of nitrogen protoxide, which is much employed as an anæsthetic, especially by dentists, by the name of "laughing-gas." The fused salt oxidizes most metals.

Nitrate of ammonia mixed with coal explodes on heating to 170°, and deflagrates when thrown on to a red-hot plate

It can also be made to explode by means of mercuric fulminate (Lobry de Bruyn, *Réc. trav, chim. des Pays-Bas*, x., p. 127). It is largely used in the manufacture of explosives.

Solid ammonium nitrate greedily absorbs ammonia, and is thereby liquefied. According to Divers (*Chem. News*, xxvii., p. 37) and Raoult (*Comptes rend.*, lxxvi., p. 1261), 100 g. of ammonium nitrate absorb at 760 mm. pressure 35 g. NH_3 at 0°, 33 g. at 12°, 21·50 g. at 18°, 23·5 g. at 28°, 20·9 at 29°, 17·5 at 30°·5, 6·0 at 40°·5, 0·50 at 79°.

Ammonium nitrate is very easily soluble in water, and deliquescent in damp air. 100 g. water dissolve at:

0°	12°	25°	30°	40°	50°	60°	70°	80°	90°	100°	
118	153	214	242	297	344	421	499	580	740	871	g. of the salt.

The solution in water takes place with considerable absorption of heat, which property is frequently made use of for cold-producing mixtures. On dissolving 6 parts of salt in 10 parts of water, the temperature sinks from +13°·6 to −13°·6. When dissolving it in water of 0°, ice is separated. The solution of 1 mol. in 200 mols. water absorbs 6·32 cals. (Thomsen).

The specific gravities of solutions of ammonium nitrate at 17°·5 C., according to Gerlach, are:—

Spec. grav.	Per cent. dissolved.
1·000	0
1·0425	10
1·0860	20
1·1310	30
1·1790	40
1·2300	50
1·2835	60

The aqueous solution of ammonium nitrate absorbs ammonia almost at the same rate as water. A solution of 74·1 g. NH_4NO_3 in 53 g. water absorbs 63·75 g. NH_3; for each gram NH_3 483 cals. are absorbed, and a solution of sp. gr. 1·275 is formed.

Absolute alcohol dissolves only 3·8 per cent. ammonium nitrate at 25°; about 100 per cent. on boiling. Methyl alcohol dissolves 16·3 per cent. at 18°·5 (Lobry de Bruyn). It is easily soluble in acetone.

Ammonium Phosphates.

The monobasic ammonium salt of orthophosphoric acid, $NH_4.H_2PO_4$, crystallizes in the tetragonal system, is isomorphous with the corresponding salt of potassium, and is less soluble than the two following salts. The dibasic phosphate, $(NH_4)_2.HPO_4$, is the ordinary commercial ammonium phosphate; it crystallizes monoclinically and effloresces in the air, with escape of ammonia. It is found in guano deposits. The tribasic salt, $(NH_4)_3.PO_4+3H_2O$, crystallizes only from an ammoniacal solution; it also gives off ammonia in the air. The phosphorus-salt of analytical chemistry (sal microcosmicum) is acid sodium ammonium phosphate, $NH_4.NaHPO_4+4H_2O$.

Ammonium Chromates.

All three chromates are known; the monochromate $(NH_4)_2CrO_4$, the bichromate, $(NH_4)_2Cr_2O_7$, and the trichromate $(NH_4)_2Cr_3O_{10}$. The last two have found application for blasting purposes. The bichromate forms large, garnet-red crystals of the monoclinic system, easily soluble in water. If lighted in one point, the decomposition rapidly progresses, with production of a strong glow throughout the whole mass, leaving a residue of green chromic oxide. The trichromate is formed from the bichromate by means of nitric or chromic acid; it forms dark red rhombic columns, which at 110° to 120° take a black-brown colour and, on being more strongly heated, detonate, leaving black chromic oxide behind.

Ammonium Chlorate, $NH_4.ClO_3$.

It is formed in small quantities in the action of chlorine on ammonia; it is prepared by double-decomposition of barium, strontium, or calcium chlorate with the carbonate or sulphate of ammonium. It forms fine needles or anhydrous columns, of burning taste, and decomposes on heating to 102° into chlorine, nitrogen, and a little oxygen. Its mixtures with organic substance explode by percussion, sometimes without external cause, with great violence. It is easily soluble in water and dilute alcohol, insoluble in absolute alcohol. Its technical application is not considerable.

Ammonium Perchlorate, $NH_4.ClO_4$.

This salt has recently found considerable technical applications, and serves for similar purposes as the persulphate, *supra*, p. 1321. It is obtained by double decomposition of barium perchlorate and ammonium sulphate. It crystallizes isomorphous with potassium perchlorate, in the rhombic system; its sp. gr. is $=1{\cdot}89$; it is soluble in 5 parts of cold water, insoluble in alcohol. On heating it splits up according to the equation:

$$NH_4.ClO_4 = Cl+O_2+N+2H_2O.$$

Ammonium Formate, $NH_4.CHO_2$.

It forms monoclinic crystals, of sp. gr. 1·266, fusing at 114° to 116°. It is easily soluble in water. On heating to 180° it splits up into formamide and water, with traces of prussic acid:

$$NH_4.CHO_2 = H_2O+NH_2.COH.$$

Ammonium Acetates.

The *neutral* salt, $NH_4.C_2H_3O_2$, forms deliquescent needles. On heating the aqueous solution to 55° it loses ammonia and passes into the acid salt. The anhydrous salt, according to Reick, fuses at 112° to 114°, splitting up into free ammonia, acid salt, water, and acetamide. The *acid* salt, $NH_4.C_2H_3O_2+C_2H_4O_2$, is much more stable and can be sublimated at 120° without decomposition; it is deliquescent in the air, soluble in alcohol, and forms addition products with alcohol.

Ammonium Oxalates.

The *neutral* salt, $(NH_4)_2C_2O_4+H_2O$, is found in Peruvian guano. It is soluble in water (at 15° in 23·69 parts) and dissociates on heating the solution. On heating the salt, it loses its water of crystallization without fusing; when more strongly heated, it yields ammonia, carbon monoxide, carbon dioxide, water, oxamide, dicyanogen, and prussic acid. It possesses no technical interest. The *acid* salt, $NH_4.H.C_2O_4+H_2O$, forms rhombic prisms, soluble at 11°·5 in 15·97 parts of water. On being heated, it fuses in its water of crystallization and is decomposed at 220° to 230°, with formation of carbon dioxide, carbon monoxide, formic acid, and oxaminic acid.

CHAPTER XIII

SOURCES FROM WHICH AMMONIA IS OBTAINED

NATURAL OCCURRENCE OF AMMONIA.

AMMONIA, especially as carbonate, is found almost everywhere in soil, water, and air, as a product of the decomposition of organic bodies, but in very slight traces. Although the growth of plants seems altogether to depend upon the ammonia thus presented to them and upon the nitrates formed by the oxidation of that ammonia (along with that formed by the electric discharge), yet this ammonia is diluted to such an enormous extent that it will ever be out of the question to recover it in substance.

In some cases rather more ammonia is collected in one spot, owing to the absorptive faculty of some kinds of clay, of peat, etc. But even in such cases it would seem hopeless to recover it in a direct way, although this sometimes becomes possible indirectly, when the materials in question are subjected to processes for recovering other useful substances, *e.g.*, peat to dry distillation, for the purpose of extracting oils and paraffin. Indeed, the principal source of ammonia, coal, seems to owe its nitrogen in a great measure to the absorptive faculty of some forms of decaying organic matter for the ammonia of air, and of that produced within its own mass.

A more direct opportunity of recovering ammonia is presented when, under favourable circumstances, the ammonium salts formed in the decomposition of organic matter are not, as usual, at once diluted and dispersed, but are allowed to collect and concentrate. Thus solid ammonium carbonate is found in the *guano deposits* on the west coast of South America, sometimes in such large quantities that it can be exported to Europe. Such ammonium salt first appeared in

Germany in 1848. The analysis of a sample proved that it consisted essentially of ammonium bicarbonate, mixed with some insoluble matter.

Native ammonium sulphate is contained in the Tuscan "*suffioni*," and forms a by-product in the manufacture of boric acid. It is also found in large quantities in the soil surrounding the lagoons, and may have been produced by the decomposition of nitrogenous organic matter in the rocks composing the Tuscan hills; but St Claire-Deville and Wöhler assume it to be formed in this case by the intervention of boron nitride. In an experiment made at Travale, four suffioni in twenty-four hours yielded 5 tons of salts, containing 3 cwt. boric acid, 1½ tons of ammonium sulphate, 1¾ tons of sulphate of magnesia, and ¾ ton of sulphate of iron and manganese. Somewhat considerable quantities of ammonium sulphate are brought into the market from this source. Ammonium chloride and free ammonia are also found in the suffioni.

Native ammonium chloride, along with sulphate, is sometimes collected in the neighbourhood of *volcanoes*, as Vesuvius and Etna. This occurrence is never of any technical importance. Sacchi and Ranieri found ammonium salts on Vesuvius; Bunsen on Hecla, principally where the liquid lava had flown over meadows, wherefore he ascribes the occurrence of the ammonium salts to the nitrogen of the plants and its absorption from the atmosphere by the porous tuff. But St Claire-Deville and other chemists believe it to be volcanically formed from hydrogen chloride, nitrogen, and hydrogen, or else from metallic nitrides. This is supported by Palmieri's discovery of ammonia in the acid-soaked scoria on the summit and in the crater of Vesuvius.

Ammonium chloride is also contained in the Stassfurt carnallite. In crude natural carnallite Diehl (*Chem. Zeit.*, 1889, p. 64) found 0·015 per cent. ammonium chloride. In artificial carnallite, such as is regularly prepared in the manufacture of potassium chloride, Neimke (*ibid.*, 1891, p. 715) found 0·8 per cent., Tröger 4·82, and Stolle (*Z. angew. Chem.*, 1891, p. 625) 3·8 per cent. Crude Leopoldshall carnallite, according to Neimke, contains from 0·09 to 0·27 per cent. ammonium chloride. Similar results were obtained by Biltz and Marcus (*Z. anorg. Chem.*, 1909, p. 183).

In rock-salt and in several descriptions of manufactured salt ammonium chloride has been found by A. Vogel (*Z. angew. Chem.*, 1891, p. 695); in apophyllite, to an extent of 0·33 to 0·51 per cent., by Freidel and Pisani (*Bull. Soc. Franç. Minér.*, 1894, p. 142), and by Lüdecke; in Scandinavian primitive rocks by Erdmann (*Berl. Ber.*, 1896, p. 710).

The source of the ammonia in carnallite is in any case a primeval marine fauna; the ammonia occurring in primitive rocks, however, is ascribed by Erdmann to some "original nitrogen" (Urstickstoff), which seems to have played a great part in the development of vegetation of those times, and perhaps also of the present time.

A little ammonia is also present in atmospheric air, in the form of bicarbonate, nitrate, and nitrite. It is widely found in the animal body, certainly in minute quantities only; and in the plants ammonia salts are so generally found that their absence must be called an exception.

For the technical production of ammonia and its salts none of these natural occurrences are of any importance; only an exceedingly minute quantity of the ammonia bought and sold comes from these sources. For our purposes we must look to the inexhaustible supply of atmospheric nitrogen, and to the combined nitrogen of bygone ages, accumulated in the coal, lignite and peat deposits, and in bituminous rocks.

The most important source of ammonia in nature is its formation in the *putrefaction* of all organic substances containing nitrogen; all the more, as also the nitrates occurring in nature probably are to the greatest extent formed through the oxidation of the ammonia evolved in putrefying processes. We can follow its formation most easily in the decomposition of urea which, as an amide of carbonic acid, needs only taking up the elements of water to pass into ammonium carbonate:

$$CO(NH_2)_2 + 2H_2O \rightarrow CO_3(NH_4)_2.$$

But also all other organic substances in the state of putrefaction yield up their nitrogen either entirely or to a great part in the shape of ammonia.

FORMATION OF AMMONIA.

Ammonia is formed in many cases where nitrogen and hydrogen meet in the nascent state, even when only one of these substances is in that state. Thus, for instance, ammonia is formed by passing a mixture of hydrogen and "nitrous vapours" (*i.e.*, a mixture of the oxides of nitrogen) through a gently heated tube, filled with porous substances, especially platinum sponge. Cold platinum sponge becomes heated to redness in such a mixture, and causes the combination of N and H to NH_3 with great violence. Especially *nascent hydrogen* causes the formation of ammonia from nitrates and nitrites, also from the free acids, but best in alkaline solution, when the hydrogen is set free by aluminium or a mixture of zinc and iron. Iron in a very finely divided state (as "ferrum reductum") reduces nitrates quantitatively to ammonia in a solution containing sulphuric acid, upon which reaction Ulsch (*Z. anal. Chem.*, xxx., p. 75) has founded a widely used analytical method. In concentrated solutions iron alone causes also the decomposition of nitrates in the presence of alkali (Lunge, *J. Soc. Chem. Ind.*, 1884, p. 287). Sodium sulphide in the presence of sodium hydrate also furnishes ammonia by heating with nitrate; the conditions of this reaction, a very important one in the manufacture of caustic soda, have been accurately investigated by Lunge and J. H. Smith (*ibid.*, 1883, pp. 460 and 525).

Atmospheric nitrogen, according to Schönbein, directly unites with the elements of water and forms ammonium nitrite,

$$2N + 2H_2O = NH_4NO_2;$$

this reaction occurs, to a slight extent, every time when water evaporates with excess of air. The combination of free nitrogen and hydrogen is accelerated by the electric spark or the silent electric discharge, but it is always very far from being complete, as the counter-reaction of decomposing the NH_3 into its elements very soon sets in. Loew (*Berl. Ber.*, 1890, p. 1443) observed that atmospheric nitrogen in the presence of caustic soda is converted by platinum black into nitrous acid and ammonia.

Ammonia is further formed by the decomposition of *cyanogen compounds* under the influence of moisture. A solution of potassium cyanate is quickly decomposed in this way:

$$KCNO + 2H_2O = KHCO_3 + NH_3.$$

The cyanides also yield their nitrogen in the shape of ammonia in contact with superheated steam; several processes for technically obtaining ammonia are founded on this reaction.

In the economy of nature, the formation of ammonia during the *decay of nitrogenous organic substances* is the most important source of that compound—all the more as the naturally occurring nitrates are undoubtedly for the most part formed by the oxidation of such ammonia. The formation of ammonia is most easily understood in the decomposition of urea, which, being the amide of carbonic acid, needs only to combine with water in order to pass over into ammonium carbonate,

$$CO(NH_2)_2 + 2H_2O = CO_3(NH_4)_2.$$

But the other organic substances in the course of putrefaction also yield part, or sometimes the whole, of their nitrogen in the shape of ammonia.

For technical purposes it is most important that nitrogenous organic substances, when heated in the absence of air, that is in *destructive distillation*, also yield up their nitrogen, at least partly, in the shape of ammonia. Although animal matters contain much more nitrogen than vegetable ones, it is a derivative of the latter, namely coal, which supplies most of the ammonia used in the arts and manufactures, when subjected to destructive distillation for the purpose of obtaining illuminating-gas and coke. But probably a very large portion of the nitrogen in coal is due to the animal remains buried in it, and to atmospheric ammonia absorbed, as we shall see later on.

We shall now treat separately of the various technical sources of ammonia.

SYNTHETICAL PRODUCTION OF AMMONIA FROM NITROGEN AND HYDROGEN.

The first attempts at producing ammonia from atmospheric nitrogen were made in the middle of the last century. In 1871, the Société d'encouragement pour l'industrie nationale in Paris offered a prize for the fixation of atmospheric nitrogen in the shape of ammonia or nitric acid. According to Birkeland's calculation, the weight of the nitrogen of the air, lying over each square kilometre of the earth's surface, is about 8 million tons, which would suffice for supplying the total wants of combined nitrogen for about twenty-five years, and the surface of the earth has an area of more than 500 millions of sq. km. These figures speak for themselves. But for the processes to be described for converting free nitrogen into ammonia, it is in most cases necessary to obtain the nitrogen in a pure state, more particularly free from oxygen. We shall first describe the processes proposed for obtaining the nitrogen in this state.

Isolation of Nitrogen from Atmospheric Air.

The proposals made for this object are partly of a chemical, partly of a physical, and partly of a combined kind. Since this matter is only of secondary importance for our purposes, we treat it only briefly. For further particulars we refer the reader to the technical literature, *e.g.*, the book of Donath and Frenzel, *Die technische Ausnutzung des atmosphärischen Stickstoffes*, pp. 11 to 38.

Chemical Processes.—These consist in removing the atmospheric oxygen by oxidizable substances, principally *copper*, leaving the nitrogen behind. The Cyanid-Gesellschaft m. b. H. (Ger. P. 218671) passes air over finely divided, red-hot copper; this is thereby converted into cupric oxide, which later on is again reduced to the metallic state. Two concentric cylinders, filled with copper, serve in turns for the oxidation and reduction, the former by blowing in air, the latter by blowing in a reducing gas. The heat produced by the reaction is utilized in both cases, and the process, once started by heating up, can be continued without supply of heat from without.

In lieu of atmospheric air, the *gases from combustions* (smoke-gases) or *lime-kiln gases* may be employed, but in these cases the carbon dioxide and monoxide must be removed, since they cause trouble, *e.g.*, in the manufacture of "lime-nitrogen" from carbide (Caro, *Z. angew. Chem.*, 1909, p. 1197).

The Nitrogen-Gesellschaft m. b. H. (Ger. P. 215608; the British patent for it is taken out by R. Riedel, No. 20631, of 1908) proceed as follows:—The smoke-gases, passed over the mixture of copper and cupric oxide, are mixed with reducing-gases or vapours, whereby the combustion process in the heating-plant is made independent of the processes going on in the Cu—CuO— mixture, and the heat of combustion is better utilized. After condensing the water, the nitrogen and carbon dioxide are separated in the well-known manner.

Very important is the observation of N. Caro, that the red-hot mixture of Cu and CuO removes not merely the oxygen, but also carbon monoxide. Therefore when employing producer-gas made from coke, or smoke-gases, there is always a product obtained containing only nitrogen and carbon dioxide which, on being passed through a solution of sodium carbonate, gives up the CO_2 and leaves pure N behind. This forms the subject of the B. P. 16963, of 1908, and the Ger. P. 204882, taken out by A. Frank and N. Caro, which runs as follows:—Producer-gas is burned by atmospheric air; the gaseous mixture formed thereby contains, besides nitrogen, an excess of O, CO, CO_2, and hydrocarbons. These gases, after being cooled down and mechanically purified, are passed through a retort, containing a mixture of metallic copper and cupric oxide. Here the oxygen is retained by the metallic copper; the carbon monoxide and the hydrocarbons are burned by the oxygen of CuO into CO_2 and H_2O. Hence the gases on leaving the retort consist merely of nitrogen and carbon dioxide; the latter is removed by absorption in the well-known way. Thus the atmospheric oxygen is completely converted into carbon dioxide, and the nitrogen remained free from carbon monoxide and hydrocarbons.

Cunningham (B. P. 25605, of 1906) burns limestone and coke in a lime-kiln. The escaping gaseous mixture of carbon dioxide and nitrogen, with a little oxygen, is passed through an ammoniacal solution of common salt, where the CO_2 is retained and practically pure nitrogen passes out.

Hurford (B. P. 19402, of 1908) employs as source of nitrogen the gases produced by burning coal-gas, petroleum, etc., which must be free from carbon monoxide, and removes CO_2, SO_2, and aqueous vapour by washing. Other patents are those of Weston (Ger. P. 279009); Bergfeld (Ger. P. 276131).

The *physical methods* for separating the atmospheric nitrogen and oxygen are on one side founded on the difference in the speed of diffusion on passing them through a membrane, on the other side on the different capacity of absorption of certain substances for the two gases, and especially on the difference in the boiling-points of the liquefied gases. The last-named process has turned out to be the most important for technical purposes.

Already Graham observed that air does not pass unchanged through indiarubber membranes, but the diffused gases are richer in oxygen; on repeating the process several times with the same quantity of air, ultimately a gas mixture containing up to 93 per cent. oxygen is obtained. Margis (Ger. P. 17981) and Leonhard Roth (Ger. P. 197393) founded special processes on that observation. The latter causes the air to diffuse immediately before its action on silicon carbide through membranes which retain the oxygen, whereupon the nitrogen is retained by the mass beyond the membranes, with formation of nitride, before the oxygen can act; the oxygen later on burns only the carbon present, and does no harm. A suitable apparatus is described in the patent specification. In actual practice a mixture of silicon carbide and iron is heated in a suitable furnace in which is inserted a membrane of burnt clay, 60 mm. thick.

Mazza (U.S. P. 1137617) separates the constituents of air and other gaseous mixtures by centrifugal action.

Mallet founded a separating process on the difference of the coefficients of absorption of oxygen (0·046) and nitrogen (0·025) in water of ordinary temperature at higher pressures, *e.g.*, 5 atmospheres.

Montmagnon and Delaire (*cf.* Donath and Frenzel, *loc. cit.*, pp. 13 and 14) found that 100 litres of wood charcoal absorb 925 litres oxygen and only 730 litres nitrogen from atmospheric air, and utilize this for separating them.

None of the just-mentioned processes seem adapted for being carried out on a large scale, except under special circumstances. But of the greatest importance are the processes based on the *fractional distillation of liquefied air*, the boiling-point of liquid oxygen being = –183°, and that of liquid nitrogen = –196°, which admits of separating them in the same way as a mixture of alcohol and water, and of benzene and toluene.

We cannot here enter on the liquefying of air by the well-known process of Linde and Pictet; we refer to their description in many technical publications, *e.g.*, Donath and Frenzel, *loc. cit.*, pp. 15 to 38. According to Linde, nitrogen can now be obtained in such a state of purity that the trace of oxygen it may contain cannot be detected by gas-analysis.

L. Roth (Ger. P. 197393, of 1908), in order to prevent the injurious effect of the oxygen in the preparation of nitrides from air, separates oxygen and nitrogen by dialyzing the air by means of a finely powdered mixture of amorphous silicon carbide (obtained as a waste product in the manufacture of carborundum) with half its weight of iron, placed on slabs of burnt clay, 2½ in. thick, built in a furnace. When forcing the air upwards through this mixture, the nitrogen passes through first and can be converted into nitrides.

R. P. Pictet (U.S. P. 1119312; Ger. P. 272675) separates air into oxygen and nitrogen by subjecting an upwardly moving stream of air to the action of a descending stream of nitrogen in a column so constructed that a succession of liquid layers is formed. In descending the liquid nitrogen dissolves oxygen from the gaseous air and becomes progressively richer in oxygen. The layers of liquid nitrogen are then caused to boil by the action of a succession of streams of nitrogen forced into the apparatus at different heights and passing to the upper end through the liquid layers without mixing therewith. These streams of nitrogen are supplied under such different pressures that the nitrogen just liquefies at the temperature of the mixture of nitrogen and dissolved oxygen at the point of entry of the nitrogen.

Jaubert (Ger. Ps. 262728, 277717), obtains pure nitrogen and oxygen by liquefying air and rectifying this.

A. Neumann (Ger. P. 281518) describes an apparatus for liquefying air and separating its constituents.

The Compagnie Internationale de l'Oxygène (Fr. P. 466315) separate liquid air into N and O by conducting it in a thin layer down over thin-coated plates of extended surface. The sole heating agent is the nitrogen escaping in the lower portion of the column by the distillation of the air.

Ges. f. Linde's Eismaschinen A.G. (B. P. 24735, of 1914) describe a vertical column-apparatus for separating the constituents of air.

Eggert (*Z. Elektrochem.*, 1915, xxi., p. 349) communicates his experiments on activating hydrogen and oxygen by means of platinum.

The preparation of pure nitrogen from air is also treated *infra*, in connection with the synthesis of ammonia by means of cyanides and cyanamides.

A number of other patents will be mentioned in the Addenda at the close of this volume.

Preparation of Hydrogen.

This is required for various purposes, one of which is the synthesis of ammonia. We enumerate some of the patents taken out for it.

Näher and Nöding (Ger. Ps. 279726, 286960) pass steam, superheated to about 1000°, successively over copper and then over iron, in a retort heated to about 800°. From the metallic oxides thus formed the metals are regenerated by means of water-gas, produced from the undecomposed steam.

The Badische Anilin- und Sodafabrik (Ger. Ps. 271516, 279852) produce it from mixtures of carbon monoxide and steam with the aid of catalyzers, such as oxides of chromium, thorium, uranium, beryllium, antimony, at temperatures not exceeding 600°. The contact masses are applied in a finely divided or porous form, preferably in sticks with a binder. They are prepared by calcining a mixture of nitrates or hydroxides at not too high a temperature. The process is also of value in removing small amounts of carbon monoxide. In gas mixtures rich in CO, the principal portion of the CO can be converted into CO_2 catalytically in another manner. *E.g.*, a mixture of 85 parts $Fe_2(NO_3)_6$ and 15 parts $Cr(NO_3)_3$ is precipitated with NH_4OH; the hydroxide mixture is dried, moulded, and then charged into the contact furnace. Already at 400° to 450°, a very energetic reaction proceeds between the steam and carbon monoxide. To the above mixture of nitrates, 25 parts of ammonium nitrate may be added. Good results are obtained with a mixture of 97 parts ferric nitrate, 2·5 chromium nitrate, and 0·5 thorium nitrate, converted by heating into the oxide mixture.

The same firm (Fr. P. 463114; the U.S. P. 1128804 is taken out by Mittasch and Schneider, assigned to the Badische) pass a mixture of hydrocarbons and steam over magnesia, covered with a catalyzer, such as nickel or nickel oxide, heated to 800°

to 1000°. The resulting gaseous mixture is freed from carbon monoxide and dioxide, leaving substantially pure hydrogen, suitable for the catalytic production of ammonia.

The same firm (B. P. 14509, of 1913, taken out by J. Y. Johnson; Ger. P. 279954; Fr. Ps. 439262 and addition 18699) purify hydrogen from sulphur by heating with a solution of caustic soda of from 10 to 50 per cent. to 150° to 225° at a pressure of 50 atmospheres.

The same firm (Ger. P. 282849; Fr. P. 459918) prepare hydrogen from carbon monoxide, or gases containing such, and aqueous vapour by the aid of catalysers, containing, besides nickel or its oxides, prevailing quantities of iron or its oxides. Their Ger. P. 284176 describes for this purpose a mixture of 3 parts cerium nitrate and 1 part chromium nitrate, dissolved in hot water and precipitated by ammonia, moulded, dried, and treated at 450° to 550° by a mixture of steam and water-gas.

Their Ger. Ps. appl. B68240, B70598, and B78324 describe nickel or cobalt chloride as catalyzers.

According to their Ger. P. 283501 (Fr. P. 453077) hydrogen is prepared by alternatively decomposing steam by metallic iron at higher temperatures and again reducing the iron oxides formed, starting from porous or spongy iron which had been obtained by reducing iron oxides or ores of any description, bedding them in coal and heating from without. An excellent material for this purpose is the "Swedish spongy iron," prepared in that way from Swedish small ore ("Schliech"), but other descriptions of iron, prepared as above, may be used as well. This spongy iron, after having been used for a short time, turns very hard, remaining, however, very porous and easily reacting. Further patents of the Badische on this subject are: B. Ps. 27955, of 1912; 8864 and 27963, of 1913; 8029, of 1914.

Their B. P. 16494, of 1914, prescribes passing gases, containing carbon monoxide, in admixture with steam, at temperatures not appreciably higher than 650° over spathic iron ore or hydroxide iron ores, preferably free from phosphorus, sulphur, or silicon, in the form of grains, or of pieces prepared by means of a binding agent, such as the hydroxide or salt of iron or aluminium.

Dieffenbach and Moldenhauer (B. P. 12051, of 1910; Fr. P. 444044; Ger. P. 270701) describe the production of hydrogen, nitrogen, or mixtures of both.

The Centralstelle für wissenschaftlich-technische Untersuchungen, Babelsberg (Ger. P. 286666; Fr. P. 469391), carry out reactions in which hydrogen is evolved under pressure and at high temperatures, *e.g.*, the synthesis of ammonia in an apparatus comprising an exterior (metallic) receiver, capable of supporting the pressure, and an interior vessel (*e.g.*, of glazed porcelain, glass, quartz, etc.) capable of resisting the chemical action and the diffusion of the hydrogen. Or they effect the reaction in an inner porous receiver which is separated from the outer wall supporting the pressure by a composition capable of resisting the chemical action and diffusion of the hydrogen.

Kausch (*Chemische Apparatur*, 1915, p. 125) discusses the recent apparatus proposed for preparing hydrogen on the large scale.

Uyeno (B. P. 11838, of 1912; Ger. P. 259530; U.S. P. 1120768) makes hydrogen by the action of hot water on an alloy of aluminium, zinc, tin, and mercury.

The Soc. l'Air Liquide at Paris (B. P. 13160, of 1914; Fr. Ps. 453187, 469854; U.S. P. 1135355, of G. Claude) makes hydrogen by compressing and cooling water-gas in heat exchangers, so that the carbon monoxide is condensed.

Messerschmitt (B. Ps. 17690, 17691, 17692, 18028, 18942, of 1913; Ger. Ps. 274870, 276132, 276919, 277500, 284532) produces hydrogen by alternate reduction and oxidation of iron ores, the heating being effected by a gas of low calorific power, and the reduction by a gas of high calorific power, employing a modification of the furnace described in B. P. 12242, of 1912.

J. L. Buchanan and E. B. Maxted (B. P. 6477, of 1914) produce hydrogen from carbon monoxide (water-gas) and steam at high temperatures by means of a catalyst composed of a lixiviated mixture of oxide of iron and sodium ferrite, reduced in a current of hydrogen and moistened with a solution of copper nitrate, whereby a copper-iron couple is formed.

Schaffer (B. P. 25710, of 1913; Ger. P. 289208; U.S. P. 1144730) obtains hydrogen by the successive oxidation of iron by means of steam and reduction of the oxide formed by means of water-gas. The first direct heating takes place with an excess of air, by which the deposition of dust, carbon, and sulphur compounds on the iron is avoided. Quite similar to this is the Ger. P. 289207.

Julius Pintsch Akt. Ges. (B. P. 28904, of 1913; Fr. P. 466739; Ger. P. 283160) obtain hydrogen from steam by passing this over hot pyrites cinders, whereby ferrous silicate is formed. As this fuses and stops up the pores of the material, compressed artificial stones of iron oxides or carbonates, and of oxides or carbonates of Mg, Ba, Sr, Al, or Ca-Mg-O are employed.

Further patents:—

Fresnaye and Suchy (Fr. P. 476454).

S. A. l'Oxhydrique française (Ger. P. 277434).

Jaubert (Ger. Ps. 272609, 272635; Fr. P. 454616).

Maschinenbau-Anstalt Humboldt (Ger. P. 253706).

The Soc. l'Hydrogène (Fr. Ps. 465474, 469489, and 472373; B. Ps. 28390, of 1913, and 6115, of 1914; U.S. Ps. 1118595 and 1129559) manufactures hydrogen by the alternate action of a reducing gas and steam upon heated ferruginous matter. To prevent accumulation of oxidizable matter introduced into the ferruginous mass by the gases employed for heating and reducing, the preliminary heating is produced by means of water-gas burnt with an excess of air, and the subsequent periodical heating with air alone. (The British, French, and American patents are taken by the Berlin-Anhaltische Maschinenbau, A.G.)

R. P. Pictet (Fr. Ps. 421838 and 421839; U.S. P. 1134416; Ger. Ps. 255733, 257715, 277115, 289065) produces hydrogen by passing acetylene through a tube, the front portion of which is heated to about 500°, at which temperature the gas dissociates into its elements with evolution of so much heat that it suffices for dissociating fresh quantities of acetylene without external heat. The rear portion of the tube is surrounded by a refrigerating appliance, and the products of decomposition, hydrogen, and lampblack are passed into a suitable apparatus for their separation. In the same way exothermic hydrocarbons, such as petroleum vapours mixed with steam, may be decomposed with the formation of hydrogen and carbon monoxide. By admitting a regulated quantity of oxygen, the combination of this with nascent carbon provides all the heat required by the reaction. The tube may be made of steel, iron, or porcelain; the conduits are preferably made of iron covered with nickel.

Bergius and Chemische Fabrik Aktien-Gesellschaft vorm. Moritz Milch & Co. (Ger. Ps. 254593, 262831, 277501, 286961) prepare pure compressed hydrogen by converting powdery metallic iron into ferroso-ferric oxide by heating with water to about 300°, whereby elementary hydrogen is set free. A high-pressure vessel, provided with a reflux cooler, is charged with powdered iron, water, and (for the purpose of hastening the reaction) a small quantity of an electrolyte, such as sodium or ferric chloride. On heating at a pressure of 300 atmospheres, hydrogen is evolved and collected in a bomb attached to the apparatus. The hydrogen thus obtained contains less than $\frac{1}{100}$ per cent. of impurities. According to their Ger. P. 286961 the action may be carried on continuously by employing water in the form of steam, at a pressure of 150 to 200 atmospheres, not above 500°.

The Farbenfabriken vorm. Bayer (Ger. P. Appl. F37834) prepare hydrogen and oxygen by means of continuous electrolysis, employing a specially constructed electrode in the form of a "channel diaphragm."

The Internationale Wasserstoff Aktien-Gesellschaft, Frankfurt a. M. (Ger. Ps. 220889 and 244733), employ pyrites cinders, after completely removing any sulphur and volatile metals by heating, for preparing hydrogen, for which purpose the cinders are specially adapted by their porosity and high fusing-point, facilitating the reduction to metallic iron. They affect this reduction by water-gas, as rich as possible in hydrogen, in perpendicular, U-shaped retorts, heated to 800° by gaseous fuel, and they obtain gas containing 98 per cent. hydrogen. This process is employed by the German and Austrian aeronautic troops. The pyrites cinders have against the otherwise used mineral ferric oxide the advantage of retaining their solidity after prolonged use, and of offering an extended surface to the action of steam, owing to their great porosity.

The Chemische Fabrik Griesheim-Elektron (Ger. Ps. 263649, 284816) prepares hydrogen from carbon or carbon monoxide containing gases, steam, and alkaline, or earth-alkaline oxides or hydroxides. Hydrogen is obtained by passing gases containing carbon monoxide, together with steam, over caustic lime or caustic soda, at temperatures between 450° to 550°. This reaction is greatly promoted by working at higher pressures and correspondingly higher temperatures. Steam, or a mixture of steam and gases containing CO, is passed at pressures from 10 to 100 atmospheres over a mixture of CaO or NaOH with coal. If merely gases containing CO are employed, good results are obtained already at a pressure of 5 atmospheres. When employing lime, the temperature should be 600° to 800°; with BaO or caustic alkali it may be considerably lower. This process is specially advantageous when passing steam over a mixture of lime and carbon at a pressure of 10 atmospheres or upwards, whereby nearly pure hydrogen is obtained. The reactions going on are:—

$$\begin{aligned} C + 2H_2O &= CO_2 + 2H_2 \\ CO_2 + CaO &= CaCO_3 \\ CO + H_2O &= CO_2 + H_2. \end{aligned}$$

Since the reactions themselves give out sufficient heat, no heat need be applied from without, if the apparatus are of sufficient size. Or else a mixture of carbon and lime is treated in a tower, first with air; the carbon serves both as a source of heat and for decomposing the steam. When the desired temperature has been attained, the air is cut off and water or steam under a pressure of 20 atmospheres are passed over the mixture on the top. The spent lime is taken out at the bottom, mixed with fresh carbon, and charged again at the top. As "carbon" especially lignite or charcoal are recommended, since these react at lower temperatures, and more quickly than coal or coke.

Further patents will be enumerated in the Addenda.

Production of a Mixture of Nitrogen and Hydrogen for preparing Ammonia.

Weise and Riche (U.S. P. 1098139, 1914; the Fr. P. 466679 is in the name of Rud. Koepp & Co.) produce sodium formate by heating caustic soda with producer-gas; in this process nitrogen escapes and is collected in a gas-holder. The formate is then converted by heating into oxalate, and the hydrogen formed thereby is mixed with the nitrogen previously obtained.

Wolf (Ger. P. 281317) also describes the preparation of a mixture of hydrogen and nitrogen.

Manufacture of Ammonia from Free Nitrogen by High Temperatures, with or without the Intervention of Catalytic Agents (except by the Aid of Electricity).

Very many proposals have been made for combining free nitrogen with hydrogen, with or without the aid of catalytic substances. In all cases regard must be had to the fact that the inverse reaction, that is, the decomposition of ammonia into its elements, by heat or electricity, takes place by the same agencies, and frequently to a much greater extent than its formation, as we shall see later on, so that some special agency must be found which favours the formation, and suppresses the decomposition of ammonia.

Ammonia can, by the action of catalyzers, at high temperatures be formed directly by the union of nitrogen and hydrogen. On the other hand, the same agents also decompose NH_3 into N_2 and H_2, so that we must write the equation:

$$N_2 + 3H_2 \rightleftarrows 2NH_3,$$

and an equilibrium must exist between those two inverse reactions for every given set of conditions. On this point several communications have been made by Nernst, and more particularly by Haber, with van Oordt, Rossignol, Jost, and other co-operators to which we cannot refer in detail (*Z. anorg. Chem*, xliii., p. 111; xliv., p. 341; *Chem. Zentr.*, 1905, ii., pp. 495 and 1300; *Ber.*, 1907, p. 2146; *Z. Elektrochem.*, xiii., p. 521; xiv., pp. 181, 373, 509; xx., p. 597; xxi., pp. 89, 128, and 241).

Bunte (*J. Gasbeleucht.*, 1910, p. 868) discusses this class of processes from the economical point of view [which since then seems to have considerably changed].

We shall now enumerate both the laboratory experiments and the proposals of inventors for practical objects in that direction.

H. Fleck[1] describes the following experiment. When hydrate of lime is brought to a red-heat, its chemically combined water is split off, and in this state it is more prone to be decomposed. If, therefore, a mixture of nitrogen and carbon monoxide is present at the same time, the following reaction takes place:—

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[1] *Die Fabrikation chemischer Produkte aus thierischen Abfällen* (Braunschweig, 1862), p. 48.

$$2N + 3CO + 3H_2O = 2NH_3 + 3CO_2.$$

This reaction was utilized by passing atmospheric air over charcoal contained in an iron tube heated to a red-heat; the issuing gas was passed through boiling water, and then through a porcelain tube filled with hydrate of lime. Whenever the latter tube was heated to a temperature "between dark red and bright red," considerable quantities of ammonia were formed (in one case 16 g. NH_4Cl from 15 cub. ft. of air); but a little above or below that temperature the evolution of ammonia was very slight, or ceased altogether. Fleck himself published his experiments only as a stimulus for further trials. Weinmann (*Ber.*, 1875, p. 977), on repeating Fleck's experiments, could not obtain any ammonia; but this may have been due to his not having hit the precise temperature required; nor was Mond (*Z. angew. Chem.*, 1889, p. 513) more successful.

Maxwell Lyte (*Bull. Soc. Chim.*, 1876, xxv., p. 427) passed a mixture of steam and nitrogen over certain alloys or other compounds of the metals of the alkalis or the alkaline earths, or zinc, namely, alloys of antimony, bismuth, arsenic, or tin with sodium, potassium, or zinc. The hydrogen liberated was supposed to unite with the nitrogen and to form ammonia.

Ed. Solvay (*Bull. Soc. Chim.*, 1876, xxv., p. 527) impregnated coke with magnesium chloride, and heated the mixture by means of a blast. The products of combustion contained sal-ammoniac, which was to be recovered by condensation. The priority of this intervention was claimed by R. Wagner (*Jahresber. d. chem. Techn.*, 1876, p. 444). [Probably any ammonia formed in Solvay's experiments was derived from the nitrogen contained in coke; *cf.* later on.]

G. Swindells (B. P., 21st June 1876) passes a mixture of air and steam over red-hot coals, and the resulting mixture of gases through a solution of caustic soda. The escaping mixture of hydrogen and nitrogen is to be converted into ammonia by heating in chambers filled with burnt clay. [In all likelihood the ammonia found by Swindells was likewise formed from the nitrogen of the coal.]

J. P. Rickman (B. P. 3341, of 1878; Ger. P. 8238) employs slanting retorts, made of iron or fireclay, of an elliptical section, filled with coke or spongy iron, and heated to about 550° C. At the lower end a mixture of steam and air is blown in; the steam is decomposed, and the free hydrogen combines with the nitrogen to form ammonia, which issues at the upper end of the retort, mixed with the excess of steam.

A modification of this proposal was patented by J. P. Rickman along with J. B. Thompson in 1880 (Ger. P. 10889). They expose coal to a slow combustion with access of air and steam in regulated quantities.

G. Th. Glover (B. P. 1890, of 1880) passes combustion-gases, containing a large proportion of nitrogen, mixed with steam and hydrochloric acid, over red-hot coals or bituminous shale. The ammonium chloride formed is to be condensed by cooling, or is passed into sulphuric acid.

To the proposals of Rickman, Thompson, and Glover, we must apply exactly the same observation as to that of Swindells. Mond (*J. Soc. Chem. Ind.*, 1889, p. 505) confirms the statement that any ammonia obtained in these cases comes from the nitrogen originally present in coal.

Serret (Fr. P. 462683) employs a mixture of carbon and alkali.

H. Endeman (*Amer. Chem. J.*, viii., p. 47) observed the occurrence of ammonium thiosulphate as a condensation product from a gas-producer in which a mixture of air and steam was forced through anthracite coal, and he believes that the sulphur was derived from the anthracite coal, the nitrogen from the atmospheric air, and the hydrogen from steam. There is, however, no proof whatever given that the coal did not contain sufficient N to account for the NH_3 formed.

G. S. Johnson (*Chem. News*, xliii., pp. 42 and 288) states that ammonia is formed if nitrogen, prepared by gently heating a mixed solution of potassium nitrite and ammonium chloride, is mixed with hydrogen and the mixture is passed over red-hot platinum sponge; or else if such nitrogen is passed over cold platinum sponge charged with hydrogen. No ammonia was formed when the nitrogen was first heated in a red-hot tube, or when it was obtained by passing atmospheric air over red-hot copper. From this Johnson concluded that nitrogen, like phosphorus, occurs in two modifications, only that formed in the cold being "active." These assertions were tested by Miss K. I. Williams and

Ramsay (*Proc. J. Chem. Soc.*, 1886, p. 223), but with a negative result. The total of "active nitrogen" found in 7·7031 litres of nitrogen prepared in the cold, as tested by the formation of NH_3, was only 0·000055 g.—that is, so slight a quantity that it must be attributed to accidental impurities not entirely removed by washing the gases. Johnson's statements were also contradicted by Baker (*Chem. News*, lxviii., p. 187).

Twinch (B. P. 3712, of 1881) passes a mixture of steam, atmospheric air, nitric oxide, and caustic-soda solution into a cylinder filled with granulated zinc. The nitric oxide takes up the oxygen of the air, whose nitrogen then forms ammonia.

According to Ramsay and Young (*cf.* Grossmann, *Das Ammoniak*, 1908, p. 2) only traces of ammonia are formed if a mixture of nitrogen and hydrogen is passed through a red-hot tube filled with iron filings.

Brunel and Woog (*Comptes rend.*, 1907, cxlv., p. 922) employ nickel oxide as a catalytical substance for forming NH_3 from air and hydrogen at a temperature of 240° to 240° C., kept up by a boiling petroleum bath.

Woltereck (Ger. P. 146712; B. Ps. 2461, of 1902; 16504, 1904; 8358, 1905; Fr. Ps. 332591 and 345390; U.S. Ps. 803652 and 803653) prepares ammonia synthetically from mixtures of hydrogen and atmospheric air by means of intermediary substances acting as oxygen carriers, such as the oxides of iron, chromium, and bismuth. The ordinary contact substances, as platinum in a finely divided form,[1] charcoal, etc. (*cf.*, however, below!), cannot be applied here, since the oxide, reduced by hydrogen, must be always oxidized again in the presence of steam. The metallic oxides are therefore mere chemical agents, being reduced at the first stage and reformed at the second stage. He operates as follows:—A mixture of atmospheric air and of gases containing free hydrogen, *e.g.*, ordinary coal-gas, more or less saturated with aqueous vapour, is passed over ferric oxide heated to a dull-red heat, preferably in the shape of rolls of iron wire, previously converted to ferric oxide. When employing ordinary coal-gas for this mixture, there is a strong formation of organic amines which must be decomposed by washing the product with strong alkaline solutions at a boiling heat, and thus forming ammonia before the gases are absorbed by acid in the usual manner. Or else a mixture of about equal parts of atmospheric air and water-gas is more or less saturated with steam and treated in the same manner by passing it over the metallic oxide at a dull-red heat. In a laboratory experiment quoted by the inventor he obtained a yield of 6·3 per cent. of the theoretically possible quantity of NH_3, when employing coal-gas as the source of hydrogen.

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[1] Therefore the process, described in Ger. P. 74275, for producing ammonium bicarbonate or formate by passing a mixture of CO or CO_2 with N, H, and steam over contact substances cannot be successful, since oxygen is absent here, as Woltereck found on putting it to a practical test.

Later on, in *Comptes rend.*, 1908, cxlvi., p. 194 (*J. Soc. Chem. Ind.*, 1908, pp. 158 and 978; *Chem. Zentr.*, 1908, i., p. 1142) Woltereck quotes some details of his experiments. When passing a mixture of air and hydrogen through water at 80° C., and then over reduced iron or the oxides of bismuth, chromium and iron at 300° to 350° C., considerable quantities of NH_3 were formed. The result is very much improved by the introduction of steam. The best results are obtained by passing a mixture of 1 part H and 78 parts air, saturated with steam at 80° C., over iron-wire gauze, first oxidized, and before the experiment again reduced by means of CO, at a temperature of 300° to 350°. Thus from 100 litres air in four and a half hours 204 mg. NH_3 were obtained. Since the iron must be again brought to the metallic state before each experiment, Woltereck now states that it is better replaced by coke or charcoal. Eighty g. coke on burning by 868 litres air, saturated with steam at 80°, furnished in forty-seven hours at 400°, 337 mg. NH_3. Four hundred and forty-one g. peat, treated in the same way, yielded even 11 g. NH_3 (8·25 g. of this being due to the peat itself, and 2·25 g. being synthetically produced from the atmospheric nitrogen). Small quantities of NH_3 were also formed when employing sugar-charcoal, free from N, at temperatures not above 700°. His British patent for this process is 28964, of 1906.

In a polemical discussion, carried on in the "Technische Rundschau" of the *Berliner Tageblatt*, especially in No. 20, of 19th May 1909, Prof. A. Frank and Dr N. Caro distinctly deny any fixation of atmospheric nitrogen in the processes of Woltereck, against whose patents they had taken proceedings for cancelling them.

Haber and Greenwood (*Z. Elektrochem.*, 1915, xxi., p. 241; *J. Chem. Soc.*, cviii., ii., p. 443) investigated the action of uranium as catalyzer in the synthesis of ammonia from its elements.

De Jahn (Amer. Ps. 1141948, 1143366) produces ammonia by passing a mixture of H and N under a pressure of 80 to 90 atmospheres at 520° to 540° over a catalyzer formed by impregnating pumice stone with nickel nitrate, igniting at 550°, heating in hydrogen for eight hours at 550°, treating the product with metallic Na, and heating with anhydrous NH_3 at 450°. Fe or Mo may replace the Ni.

The same inventor's Amer. P. 1141949 prescribes for the same process catalyzers formed by igniting a salt of Co, Mn, Ti, Ce, Be, U, or Si upon a carrier of pumice, reducing the product in H, and heating with metallic Na and anhydrous NH_3 at 300°. His U.S. P. 1151537 describes a catalyzer formed by heating sodium or potassium on pumice at 550° to 660°.

Andriesen and Scheidemantel (Ger. Ps. 284341 and 285111) employ the electric light-arc for the combination of N and H to ammonia.

Production of Ammonia by the Process of Haber.

A new epoch for the production of ammonia from its elements sets in with the labours of F. Haber and his co-operators, which have led to a complete technical solution of that problem, after they had entered into connection with the Badische Anilin- und Sodafabrik at Ludwigshafen, which concern lent its enormous material and spiritual powers to that object.

We shall give a short digest of the work of Haber and Le Rossignol, based upon a report made by them in the spring of 1909 to the Badische, and published (with omission of some points required by business reasons) in the *Z. Elektrochem.*, 1913, pp. 53 *et seq.*; 1914, p. 297; 1915, p. 89. A former paper by Haber is found in the same *Z. Elektrochem.*, 1910, p. 244.

To begin with, they point at the importance of the task in question. The consumption of ammonia amounts to several hundreds of thousands of tons, which up to that time were almost entirely obtained from the nitrogen of coal. Ammonia, in the shape of 25 per cent. ammonium sulphate, has a value of 89 Pfennig per kilogram, whilst the value of the nitrogen contained in it can be put at 2½ Pfennig, that of the hydrogen at

17½ Pfennig, altogether only 20 Pfennig. This assumes the nitrogen to be prepared by fractional distillation of liquefied air, or by the alternate action of air and producer-gas on hot copper; but in other cases—*e.g.* in the preparation of formic acid from producer-gas and caustic soda, or sodium salts and lime—large quantities of nitrogen are obtained as a worthless by-product. (Nitrogen free from argon, or nearly so, as it is obtained from liquid air, is more valuable for the synthesis of ammonia than nitrogen containing a relatively large proportion of argon.) Hydrogen is obtained on a large scale by various methods, *e.g.* in the production of calcium hypochlorite by electrolysis of sodium chloride, and in many other processes, where it is utilized in the best case for heating purposes.

The attempt at producing ammonia from the elements is rendered difficult by the fact that at ordinary temperatures (at which the thermodynamic equilibrium under ordinary pressures would allow of a nearly complete union of the elements), they cannot be brought to combine; whilst at a bright red heat where this easily takes place, the reaction stops after a minimal percentage has been formed, because traces of ammonia in the most favourable gaseous mixture suffice for producing the thermodynamic equilibrium. Haber and van Oordt (*Z. anorg. Chem.*, 1905, xliv., p. 342) have worked this out for a temperature of 1000°. [For the mathematical deductions we must refer to the paper of Haber and Rossignol.]

For technical purposes not merely the position of the equilibrium, but also the velocity with which it is reached, is of the greatest importance. If large quantities of the catalyzer are employed, and the gases are left for a long time in contact with it, much lower temperatures can be employed than in the opposite case. The authors show why the practical limits of temperature are between 500° and 700°. The results are all the more favourable the higher pressures are employed. The task of producing pressures of 200 to 250 atmospheres in gases and manipulating them under these pressures has been long ago solved by practical means. The authors give formulæ and diagrams, showing the thermodynamically possible percentages of ammonia at various pressures and temperatures. They show that in no case it is practicable to pass the compressed gases over the catalyzer, to absorb the ammonia formed, and to allow the remaining gases to escape. The latter must be carried back over the catalyzer, and a circulation must be produced, preferably always under pressure.

Further considerations show that the separation of the ammonia formed under high pressure is easiest by reducing it to the liquid state, but not allowing it to solidify, which is possible by cooling the gases down to −75°. Even then some ammonia is left in the gases, but is not lost, as the gases are again passed over the catalyzer.

Concerning the furnace for carrying out the reaction, the authors, after mentioning their first attempts with quartz tubes (which do not admit of working over 50 atmospheres), describe the apparatus finally adopted. It is a steel cylinder of special shape, with an electrical inside heating arrangement. An apparatus on similar principles was employed for working on a large scale; this is described in detail and illustrated by diagrams; also an apparatus for working without circulation of the gases.

They then proceed to describe their experiments with various catalyzers. They first worked with *cerium* and its congeners, in quartz tubes at a pressure of 50 atmospheres, at temperatures up to 700°, then with *manganese*, under the same conditions; with *tungsten;* with *uranium* of various qualities (which gave surprisingly good results, *vide supra*, p. 1070, the paper by Haber and Greenwood); and, with *ruthenium and osmium*, which proved most efficient catalyzers, yielding up to 5·5 and 9 per cent. of NH_3.

The subject of the combination of elementary nitrogen with oxygen and hydrogen is treated from a general point of view in a lecture, held by Professor Haber before the German Chemical Society at Berlin on 26th March 1913 (extract in *Z. angew. Chem.*, 1913, iii., pp. 323 *et seq.*), from which we give a short extract. He first discusses the requirements of the world for supplying nitrogen compounds to the soil, to make up for that taken out of it for agricultural and technical purposes. The stock of nitrate of soda in Chile will last about another fifty years. The nitrogen contained in the coal consumed (about 1 per cent. of its weight) is lost, if the coal is burnt as such; it could be partly recovered, if all the coal were previously converted into coke, collecting the by-products formed; but although this process extends more and more, there is no prospect under the practically existing conditions of supplying thereby the constantly increasing requirements of the ammonia market; nor is this the case with the process of Mond, which yields 70 per cent. of the nitrogen of coal in the shape of ammonia, but which cannot be generally applied. Therefore for several decades past numerous attempts have been made at solving the problem in quite a different way, by combining atmospheric nitrogen with oxygen or hydrogen. The combination of N with O need only go up to the production of NO, since this is readily converted into nitric acid. Haber discusses in detail, both the theoretical point of view and the practical attempts made in this direction which do not belong to the present chapter, and then passes on to the combination of nitrogen with hydrogen, attempted in various ways, more particularly by the catalytic action of various metals, some of which have the drawback of losing their activity after some time. His own experiments in this direction showed that the best results are obtained with chromium, iron, manganese, and nickel, and more particularly with osmium and uranium (the latter preferably in the shape of its nitride). The Badische Anilin- und Sodafabrik, which had taken up to Haber processes for technical exploitation, made many valuable additions to them, and succeeded in replacing those expensive metals, osmium and uranium, by specially treated base metals; the difficulties in the construction of furnaces were overcome, and what is most important, the preparation of hydrogen for this purpose by electrolysis was replaced by its production by means of coal.

The subject in question is also treated in Haber's Hurter Memorial Lecture, held at Liverpool, 26th November 1913 (printed in *J. Soc. Chem. Ind.*, 1914, xxxiii., pp. 49 *et seq.*).

Haber's Researches on Ammonia, more especially on the equilibrium of its formation from the elements, on the heat phenomena in this reaction, and on the specific heat of gaseous ammonia, are found in *Z. Elektrochem.*, 1914, p. 597, and 1915, pp. 89, 206, 228, 241.

A further lecture on this subject was delivered by Haber in June 1914 (*Z. angew. Chem.*, 1914, pp. 473 *et seq.*). He shows that from thermodynamical considerations the mixture of N and H is best made in stoechiometric proportions, and what led him to employ the temperature and pressures, and the catalyzers, indicated in his former publications. He refers to the further work done in this field by the chemists of the Badische Anilin- und Sodafabrik, after the process had been taken over by them, more especially by Dr Bosch and Dr Mittasch, with the result that much less costly catalyzers may be employed, if special methods are used for preparing them, for removing certain impurities, and for greatly improving their action by the admixture with other badly or not at all catalyzing substances. The transference of the laboratory experiments of Haber (who mentions Le Rossignol as his principal co-operator) to the erection of large works at Oppau, near Ludwigshafen, has been principally effected by Dr Bosch, of the Badische, who also succeeded in overcoming a serious difficulty occurring in large-scale works, viz., the cracking of the steel tubes through a prolonged action of the hot compressed gases.

According to *Chem. Zeit.*, 1910, p. 345, Haber and Rossignol, by employing *osmium* and *uranium* as catalyzers at temperatures between 500° and 550°, and at a pressure of 200 atmospheres, succeeded in converting 8 per cent. of the mixture of nitrogen and hydrogen into ammonia. This was liquefied by cooling under pressure, and the remaining mixture of N and H, after heating up, was again passed through the contact mass. Since the hydrogen can be cheaply obtained from water-gas, and the mechanical force required is comparatively small, nor is the requisite temperature very high, that process, in opposition to the production of atmospheric nitre and of lime-nitrogen, is not confined to places where hydraulic power is cheap. It can be carried out everywhere where the coal is cheap enough for producing water-gas.

Haber (*loc. cit.*) points out that *osmium*, at the temperature and pressure indicated by him, has an excellent catalytic action; but since the total stock of that element, existing on the earth, does not essentially exceed 100 kg., "another transferring medium had to be sought for, and was ultimately found in the shape of *uranium*, which is easily obtained by heating uranium oxide and carbon in the electric arc, and which is extremely active already at temperatures below 500°. The use of osmium in that case is protected by Ger. Ps. 223408 and 272637 of the Badische. Clean asbestos is saturated with a solution of potassium osmate, so that after drying and reducing the osmium to the metallic state, from 5 to 10 per cent. of it adheres to the asbestos; the alkali present increases the catalytic action. The British patent for these catalyzers is 14023, of 1910; the American patent 999025; the French patent 417940.

A most important feature of the Haber process is the low consumption of energy required by it. The *J. of Gas Lighting* (quoted from *Chem. Trade J.*, 1915, lvi., p. 527) gives the following figures in units of current per kilogram of fixed nitrogen:—

Birkeland-Eyde's process for manufacturing "Norge saltpetre" (Lunge, *Sulphuric Acid and Alkali*, 1913, i., p. 232)	62 H.P.
Process of Schönherr, of the Badische Anilin- und Sodafabrik (Lunge, *eod. loco*, p. 239)	59 "
Frank and Caro's "Lime-Nitrogen" process, this volume, p. 1128	24 "
Serpek's Aluminium Nitride process, this volume, p. 1102	12 "
Haber's process	2 "

This comparison shows that the two first-named processes are financially remunerative only where large quantities of electricity are to be had at a very low figure, *i.e.*, in the neighbourhood of waterfalls. The next two processes are applicable in places where cheap electricity may be generated as a by-product, *e.g.*, where power-gas is used. But the Haber process consumes so little energy that it can be worked wherever combustibles are to be had at normal prices. A low cost of hydrogen is essential for it; the new productive methods make it possible to make hydrogen for about 1s. per kilogram, or about 2s. 6d. per 1000 cub. ft., which means a cost-price of 3d. per kilogram of gaseous ammonia, against its market value in normal times of about 11d. per kilogram. Moreover, the ammonia produced by it is of a high degree of purity, and is therefore specially adapted for Ostwald's and other processes of producing nitric oxide from NH_3 catalytic action (Lunge, *loc. cit.*, pp. 253 *et seq.*).

The following patents have been taken out by Haber:—

Ger. P. 229126 describes the employment of *uranium* as catalyzer for the synthesis of ammonia from nitrogen and hydrogen, in the metallic form or in that of alloys and nitrides, also mixed with indifferent substances (graphite, clay, asbestos, quartz, metals) or other catalyzers. This action is already strongly pronounced at temperatures below 500°; it is best promoted by high pressures.

His Ger. P. 235421 states that, in spite of the unfavourable equilibrium and the insufficient catalytic power of the contact substances, the technical production of ammonia from the elements is possible by subjecting the mixture of N and H *under permanent pressure* in turns to the catalytic formation of ammonia at higher temperature, and taking out the ammonia by absorption or condensation at lower temperatures, taking care to transfer the heat of the gases after the reaction to the gases remaining after the removal of the ammonia, before again subjecting them to the reaction.

The Fr. P. 406943 states that it is sufficient to work continuously under high pressure, without recovering the heat produced by the reaction.

His Ger. P. 238450 states that the reaction is best produced at pressures from 150 to 250 atmospheres, and upwards.

Haber's Ger. P. 259996 (B. P. 61, of 1911; U.S. P. 1149510, with Bosch and Mittasch) describes as catalyzers for combining nitrogen and hydrogen to ammonia *tungsten*, as well as its alloys and nitrogen compounds. Commercial tungsten, as it is obtained by reducing the ores at high temperatures, gives very bad yields, but it is quite different with tungsten or its nitrides, prepared from pure tungsten compounds at temperatures not essentially exceeding 600°. His Ger. P. 260756 states that higher temperatures than 600° can be employed for the reduction of tungsten, if ammonia is employed as the reducing agent, which admits of working much more quickly. (Tungsten as catalyzer is also prescribed in the Ger. P. 254934 of the Société Générale des Nitrures, of Paris.)

The substance or the later work of Haber and his co-operators is contained in the patents of the Badische Anilin- und Sodafabrik, and it is at the present time not possible to extricate the results obtained by him from those obtained by the chemists of the Badische.

B. P. 12977, 1913; Fr. P. 411446; and U.S. P. 971501 by Haber and Le Rossignol, protect the use of *osmium* or *ruthenium* salts as catalyzer for NH_3.

In 1912 the Badische ordered Linde ice-machines for that purpose for £50,000. According to A. Frank (*Chem. Zeit.*, 1914,

p. 1261) the process was carried out at the rate of 36,000 tons ammonia per annum. In the year 1915, according to P. F. Frankland, 130,000 tons sulphate of ammonia was to be made by the Haber-Badische processes.

The synthesis of ammonia by the Haber process, and its further development by the Badische Anilin- und Sodafabrik, is the subject of a lecture given by Professor Bernthsen, one of the directors of that factory, at New York, on 11th September 1912, and published in *Z. angew. Chem.*, 1913, pp. 10 *et seq.* After describing the work previously done by Haber and his coadjutors, he gives an account of the tasks solved by the Badische, beginning at 1908, especially by Dr Bosch and his co-workers, in order to introduce the Haber process into practice on a large scale. The principal points were: the construction of apparatus enabling to work at enormous pressures, and at the same time at temperatures where both the mechanical strength and the chemical resistance of iron and steel are greatly diminished; the separation of the ammonia from the gases; and more particularly the selection of sufficiently powerful catalytic agents, and their improvement ("activation") by other substances mixed with them, which probably form a sort of skeleton within the mass of the catalyzer, and prevent its surface from being diminished during the process. The powerful but most expensive catalyzers—tungsten, osmium, uranium, etc.—could thus be replaced by iron, manganese, or molybdenum. Further studies were made concerning the "contact poisons," which are partly quite different in this case from the "poisons" in the manufacture of sulphuric acid. To the "contact poisons" in the synthesis of ammonia belong—*e.g.*, sulphur, selenium, tellurium, phosphorus, arsenic, boron, the hydrogen compounds of S, As, and P, some hydrocarbons, lead, bismuth, tin. Very poisonous are the oxides of sulphur, *e.g.*, SO_2. Extremely small quantities of these substances, such as are nearly always contained even in the "chemically pure" commercial articles, and in so-called "pure" gases, may essentially reduce or even annihilate the action of ammonia catalyzers. Thus, *e.g.*, iron made from technical ferric oxide, containing 0·1 per cent. sodium sulphate, is usually quite inactive. Iron, containing 0·1 per cent. sulphur, is generally useless, and even such containing 0·01 per cent. S is greatly inferior to absolutely pure iron. The information gained on this point led to work at two tasks, viz.—(1st) the preparation of contact masses free from poisons; (2nd) the removal of all contact poisons from the gases to be combined. As little as one-millionth of sulphur in the gases is injurious, and even electrolytic hydrogen must be specially purified, let alone hydrogen made from water-gas. An important part is played by the impurities taken up by the gases from the iron of the apparatus, from the lubricating oil, etc. The negative results of former workers when employing base metals as contact substances (Wright, Ramsay and Young, Neogi and Adhicary) are reducible to the impurities contained in the metal and gases. The information on the part played by the most various substances as "activators" and "poisons" in the synthesis of ammonia, gained by thousands of experiments made at the Badische works, especially by Dr Mittasch, has now created a solid foundation for establishing the conditions of manufacturing ammonia on the large scale permanently, and with good yields. Lastly, the question had to be studied how to obtain the two initial gases in the best way. For nitrogen this was comparatively easy, starting from atmospheric air, removing the oxygen either by physical means (Linde's process), or by red-hot copper, burning hydrogen, etc. Hydrogen can also be obtained in various ways, all of which were, of course, carefully studied. Anyhow both these gases are available in every quantity, and sufficiently cheap; nor is this depending on the presence of great water power, like the industry of calcium nitrate. Finally, Bernthsen shows by statistics (*cf.* Chapter XIV.), that very considerable quantities of synthetic ammonia may be thrown upon the market, owing to the regular expansion of the consumption of this article, without damage to the other sources of ammonia and its salts.

According to Hempel (*Z. angew. Chem.*, 1915, i., p. 145) the Badische now manufacture 140,000 tons sulphate of ammonia per annum by Haber's process. A petition addressed to the German Reichstag by the Verein zur Wahrung der Interessen der chemischen Industrie Deutschlands in May 1915 (*Chem. Ind.*, 1915, p. 189) states that by the end of this year 75,000 tons of 100 per cent. ammonia, equal to 300,000 tons ammonium sulphate, will be produced per annum by the Haber process, equal to about half the quantity of nitrogen compounds imported into Germany from abroad for agricultural purposes. All the raw materials required for this (air, water, coal, calcium sulphate) are at disposal in the country in ample quantities.

The patents taken out by the Badische Anilin- und Sodafabrik in this matter are:—

B. Ps. (taken out by J. V. Johnson on their behalf) 2414, of 1908; 2525, 17642, 30380, of 1909; 5361, 5382, 10441, 13097, 15973, 17951, 19249, 19250, 19251, 20127, of 1910; 61, 5833, 5834, 5835, 5836, 12662, 21151, 24657, 25252, 26749, 28167, of 1911; 3345, 9841, 9842, 25259, 26770, 27955, 28200, of 1912; 8864, 12977, 24823, of 1913.

Ger. Ps. 203750, 223408, 234129, 235300, 235421, 235765, 235766, 235868, 236342, 236395, 236892, 237436, 238450, 241510, 243839, 246377, 246554, 247852, 249447, 250377, 252275, 254006, 254344, 254437, 254571, 256296, 256855, 258146, 259647, 259648, 259649, 259702, 259870, 259871, 259872, 260010, 260992, 261507, 262823, 263612, 265294, 265295, 265296, 268929, 269819, 270192, 272637, 273315, 275156, 276133, 276304, 276305, 276490, 277526, 279582, 279954, 281926, 284176, 285703, 286430.

Fr. Ps. 387002, 405712, 406943, 411446, 416877, 417940, 418059, 418287, 418289, 418425, 418434, 425099, 429696, 431295, 436472, 439261, 449010, 456963, 458218, 459918, 466303.

U.S. Ps. 957842, 957843, 993144, 990191, 990192, 1006206, 1118628 (Bosch and Mittasch); 1119948 (Pier); 1027312, 1053951, 1053952, 1083585 (Bosch and Mittasch); 1089185, 1094194, 1152930 (Bosch, Mittasch, Wolf, and Stern); 1128843 and 1148570 (Bosch and Mittasch).

We now give a short digest of the patents of the Badische Anilin- und Sodafabrik:—

Their Ger. P. 254437 prescribes heating the metals, oxides, carbonates, etc., to be used as catalyzers, in the presence of air or oxygen, or otherwise, in such a way that the resulting products consist essentially of oxides, which are eventually reduced. Exceedingly small amounts of impurities, such as are mostly present in commercial "pure" iron preparations, suffice for essentially raising and prolonging the action of the contact mass.

Their Ger. P. 254344 prescribes purifying the gases, to be catalytically combined by base metals, from sulphur, phosphorus, arsenic, or their compounds, and carbon monoxide, which act very injuriously in the catalytic process. According to Ger. P. 259871, water and water-forming substances should be completely removed before the catalysis.

Their Ger. P. 254571 treats of the precautions to be observed when working with hydrogen at high temperatures, *e.g.*, in the synthesis of ammonia, by coating the inside of the reaction vessels with a substance chemically indifferent to hydrogen, and allowing the hydrogen to pass through without much resistance. It has been observed that on working with hydrogen under pressure in hot iron apparatus, these after some time lose their mechanical strength; and after some time even the outside shell is injuriously affected. This is caused by the fact that the hydrogen at high temperatures and pressures reacts on the carbon chemically combined with iron. This must be avoided by employing as material for the vessels iron free from carbon, or nickel, silver, etc. An addition to this is made in Ger. P. 256296.

The B. P. is 20127, of 1910.

Their Ger. P. 223408 describes the application of *osmium* as catalyzer for ammonia. Ger. P. 272637 prescribes precipitation of the osmium on the substratum from the alkaline osmates. The presence of alkali increases the catalytic action.

The Ger. P. 247852 of the Badische indicates as catalyzers for the synthesis of ammonia from the elements, *metallic iron* or *iron nitride*, produced from its compounds, at temperatures not exceeding 600°. Pure ferric oxide or ferroso-ferric oxide is put into the contact tube, and the mixture of N and H passed over it at temperatures not exceeding 600°. The best results are obtained by employing as contact mass pure iron or iron nitride, prepared at temperatures not exceeding 600° from ferric oxide, which had been produced by heating pure iron in the presence of oxygen, or by heating ferric oxide up to the fusing-point; or by repeating the successive oxidation and reduction several times, in which case the low temperature (600°) need only be used at the last reduction. The Fr. Ps. are 406943 and 436472; B. Ps. 24657 and 25252, of 1911; 9841 and 9842, of 1912; U.S. P. 1083585.

According to Ger. P. 256855 the iron or iron nitride may also be produced at temperatures above 600° (which causes a great saving in time), if during the reduction more undecomposed ammonia is present than corresponds to the conditions of equilibrium at those higher temperatures. This is again mentioned in a German patent, where the temperature for the reduction of iron is put = 800° to 900°.

The U.S. P. of the Badische, 1006206, describes the catalytic production of ammonia by means of reduced iron at pressures from 180 to 250 atmospheres. Their Fr. P. 429696 also employs base metals, purified and made available for catalysis by the addition of appropriate compounds.

The *hydrogen* serving for this purpose is previously purified from sulphur, phosphorus, arsenic, from compounds of these elements, and from carbon dioxide by means of alkaline solutions, especially in a heated state and under pressure—*e.g.*, by caustic-soda solution of 10 to 15 per cent. NaOH, at 150° to 225° at a hydrogen pressure of 50 atmospheres.

The Fr. P. 425099 of the Badische describes as substances to be added to iron as a catalytic agent, which greatly increase the yield of ammonia; the other elements of the iron group, and the oxides, hydroxides, and salts of the *alkali*, and *alkaline earth* metals; but compounds which can give rise to the formation of sulphur, selenium, tellurium, phosphorus, arsenic, boron, etc., under the conditions of synthesis, are to be avoided as catalysts. An addition to that patent, dated 24th May 1912, prescribes selecting substances which contain or fix hydrogen, and those which contain or fix nitrogen. The U.S. P. 1118628 of Bosch and Mittasch, and U.S. P. 1148570 of Bosch, Mittasch, and Wolf, transferred to the Badische, describe the same invention.

Their Ger. P. 262823 quotes, as catalyzers *cerium*, mixed with 2 per cent. potassium nitrate; *osmium* or osmium hydroxide, with 10 per cent. potassium osmate; *barium* + 3 per cent. potassium nitride; *lithium* as metal, hydride or nitride, with 3 per cent. potassium nitrate; *thorium* or *aluminium* + 1 to 3 per cent. potassium nitrate.

Fr. P. 416877 describes *uranium* (as metal, or alloy, or nitride, etc.) as catalyzer for NH_3.

B. Ps. 19249, of 1910; 21151, 28167, of 1911; 3345, of 1912, and Fr. P. 425099, describe various catalyzers, as Mo, Pd, Li, Mg nitrides.

The U.S. P. 1119948, by M. Pier, transferred to the Badische, prescribes as catalyzer *ruthenium* compounds, such as K_2RuO_4, $KRuO_4$, or $Ru(OH)_3$, heated to 450°, under 80 atmospheres' pressure, or more. A yield of 11 to 12 per cent. NH_3 by volume is obtained, using 80 atmospheres' pressure.

The B. P. 19249, of 1910; Ger. P. 249447 of the Badische, enumerate a great number of *promoters* to the catalytical action of iron, nickel, and cobalt for ammonia; viz., compounds of Mg, Be, Al, K, Na, Ba, Sr, Ca, or rare earth metals, of Zr, Va, Ta, Cr, Mn, Mo, W. The addition of the oxide or other compounds of Mg or Al is particularly favourable.

Their Ger. P. 276133 treats of cases in which "promoters" are present at the same time with *contact poisons*. The action of the latter can be prevented or greatly reduced by working at the lowest possible temperature.

Their Ger. P. 281926 states that when using large-sized apparatus, and especially efficient catalysts, the yields may be reduced through too great an amount of heat being produced. This is avoided by cooling, *e.g.*, by means of a serpentine, placed in the contact mass, traversed by cold gases.

Their Ger. P. 277526 points out that the ammonia, catalytically prepared under high pressures, even after being absorbed by water under pressure, and driven out again, is more or less contaminated by hydrogen and nitrogen, which have an injurious action in some cases. These are removed by fractional distillation of the impure liquid ammonia under pressure.

According to their Ger. P. 279954, the removal of the sulphur compounds contained in the hydrogen is most quickly, safely, and completely affected by treating the hydrogen or the gas mixture containing it with alkaline liquor at a high temperature under pressure.

Their Ger. P. 279582 states that in lieu of *cerium*, its *carbide* (which is cheaper and more easily accessible than the metal, and which can be prepared from a mixture of cerium oxide and coal in the electric furnace) may be employed as catalyzer. Its action can be increased by "activating" with oxides, hydroxides, or salts of the metals of the alkalis, alkaline earths, or earths.

Molybdenum and its nitrides are described as catalyzers for NH_3; their preparation is described, and suitable additions to them are mentioned in B. Ps. 61 and 12662, of 1911.

Their Ger. Ps. are 246554, 250377, 259647, 259648, 259649, 260010; Fr. P. 431295.

Various improvements of the process are enumerated in Ger. P. 260992.

Ger. Ps. 249447, 258146, 261507 describe various additions which can be made to contact substances, especially to *metallic iron.*

Ger. Ps. 234129, 236342, 236892, 241510 describe *silicon nitride* as catalyzer for ammonia, mixed with various other substances; Fr. P. 405712; U.S. P. 993144.

Ger. Ps. 235300, 235421, 235765, 235766, 235868, 236342, 236395; Fr. P. 418425; U.S. P. 1027312, describe *aluminium nitride* for that purpose.

Ger. P. 254006 states that when employing *manganese* metal as catalyzer for ammonia, the mixture of N and H must be previously entirely purified from oxygen in the free or combined state (*e.g.*, as water).

Ger. P. 243839 describes the preparation of *aluminium nitride* as catalyzer for NH_3; Fr. Ps. 418059 and 418425; B. P. 5382, of 1910.

Ger. P. 237436 describes the purification of the nitrides of silicon, aluminium, titanium, zircone, beryllium, etc.

Ger. P. 203750 describes the preparation of *titanium* nitrides by heating titanic acid with charcoal and sodium sulphate in a current of nitrogen. Ger. Ps. 202563, 203748, 204204, 204475, 204847 describe the production of ammonia by means of these nitrides.

B. Ps. 2414, of 1908, and 2525, of 1909; and Fr. P. 387002, refer to the same subject; also U.S. Ps. (by Bosch), 957842, 957843, 990191, 990192.

Ger. P. 277526 describes the preparation of *pure liquid or gaseous ammonia* from that obtained by contact processes, and absorbed by water under pressure, by means of fractional distillation under pressure. B. P. 25259, of 1912; Fr. P. 458950.

Ger. P. 270192 describes the separation of synthetically produced ammonia, by passing it, together with the absorbing liquid, through pipes, employing systematically absorbents of diminishing contents of ammonia.

Ger. P. 275156 prescribes cooling the iron or steel of the vessels, in which ammonia is produced by synthesis from the elements, down to 450°, which admits of working under pressures of 30 atmospheres and upwards, and with any description of iron or steel.

Ger. P. 281926 describes a cooling-worm within the contact mass itself, in order to prevent it from getting superheated.

Fr. P. 418434 prescribes condensing the catalytically prepared ammonia to the solid or liquid state in the reaction vessel itself by cooling the walls thereof. The B. P. is 13097, of 1910.

Tungsten is described as a catalyst for ammonia in their Fr. P. 439261; B. P. 1161, of 1912; Ger. Ps. 246554, 259647, and 286430.

Fr. P. 449010 prescribes *depriving the gaseous mixture* before catalysis *of water* and substances capable of yielding it, preferably by passage over heated palladium asbestos and then over quicklime. The yield of NH_3 is thereby increased. The B. P. is 22352, of 1912.

B. P. 5835, of 1911; Amer. Ps. 1068966, 1068967, 1068968, 1068969, enumerate catalysts consisting of an alkali metal, alkaline-earth metal, or members of the group Mn, Wo, Mo, Os, Ce, Ta, Ni, etc., and "promoters" in the shape of oxides or other compounds of the alkali metals; and to the "contact poisons" are added easily fusible and reducible metals, such as tin and lead.

B. P. 28200, of 1912, prescribes protecting the iron vessels in operating with hydrogen under high pressure and at a high temperature, *e.g.*, in the synthesis of ammonia by interposing an atmosphere of nitrogen between the hydrogen and the wall of the vessel.

U.S. P. 1054901 (Bosch and Mittasch) describes the preparation of silicon nitride (Fr. P. 405712).

B. P. 26770, of 1912, describes the preparation of hydrogen for the synthesis of ammonia by causing carbon monoxide and steam to interact at 300° to 600° under a pressure of 4 to 40 atmospheres in the presence of a catalysator such as iron, nickel, and the like, with the production of CO_2 and hydrogen, and removing the former by absorption.

Fr. P. 425099; Amer. P. 1094194, enumerate a great many substances serving as "promoters" in the synthesis of NH_3 by means of iron as catalyzer.

Fr. P. 459918; B. P. 27955, of 1912; 8864, of 1913, give details on the production of hydrogen from water-gas by catalytical means.

Fr. P. 466305; B. P. 24823, of 1913, prescribe cooling the gases by means of a water-coil.

B. P. 15973, of 1910; Fr. Ps. 418287 and 418434, describe vessels for the synthesis of NH_3 from the elements under pressure.

Ger. P. 285703 prescribes the employment of a mixture of water-gas with gases containing a higher percentage of carbon monoxide.

Further Processes for producing Ammonia by Synthesis from its Elements.

The Farbenfabriken vorm. Bayer & Co. (B. P. 16903, of 1913; Fr. P. 460859; Ger. Ps. 285698, 286719) in the manufacture of ammonia from its elements obtain a very good yield by allowing the mixture of H and N to act under high pressure upon substances which absorb N or H, or both gases, and then allowing the gas mixture to expand.

Peacock (U.S. P. 1092167) prepares a hydride of iron, *e.g.*, FeH_3, by treating spongy iron with hydrogen, and exposes this to the action of nitrogen, free from oxygen or readily reducible oxygen compounds, at a temperature at which the hydride gives off nascent hydrogen, which combines with the nitrogen to form ammonia. At the same time hydrogen is supplied to reconvert the lower hydride continuously into the higher hydride. The U.S. P. 1129504 describes the formation of phosphorus nitrides, which on treatment with steam yield ammonium phosphate.

Bender (Ger. P. 277435) supplies water continuously to the porous walls of a gas-producer. The steam, or its elements, diffuses through the walls into the furnace, where the nascent hydrogen and oxygen combine with the nitrogen present in the combustion gases, whereupon the gases are suddenly cooled. The pressure within the furnace is one or several atmospheres above normal. According to his Ger. P. 279007, he obtains compounds of nitrogen with oxygen and hydrogen by burning combustible materials with air under increased pressure, adding up to 1 kg. water for 1 kg. of burned C in the form of spray, which is to a great extent decomposed, and cooling the gases as above by means of a hollow grate. The yield increases with pressure. At 2000° about 1 vol. per cent. NO and 0·25 vol. per cent. NH_3 are formed; the gases issuing contain ammonium nitrite.

Bambach (Fr. P. 469331) produces ammonia by synthesis by means of a gas-producer, operated with air in the normal manner, but with a charge of fuel which has been treated with metallic salts, oxides, hydroxides, or carbides. Metallic nitrogen compounds (cyanides, cyanamides, nitrides, etc.) are thus formed, and are decomposed *in situ* by steam or atomized water, so as to produce ammonia which is carried forward by the gaseous current and oxides or salts which are recovered from the ash. The air is preferably preheated, and the gases containing NH_3 are chilled by a cooling coil in the centre of the producer, surrounded by an iron drum connected with an exhaust. Small proportions of magnesium chloride, calcium fluoride, etc., may be added to the charge to increase the yield of ammonia and the speed of the reaction.

The Société Générale des Nitrures, of Paris (B. P. 11091, 21366, and 22586, 1913; 4287, 1915; Ger. P. 238340; Fr. Ps. 476121, 474330), treat a mixture of bauxite and carbon in an electric furnace, remove the ferro-aluminium thus formed, and expose it in the moist state to air, whereby the mass gets spontaneously heated, even up to 2000°, without any external heating, a compound of Al and N being formed. This impure aluminium nitride may be either utilized directly as manure, or for producing ammonia and alumina by the well-known process. Their Ger. P. 254934 prescribes *tungsten* as a catalyzer.

L. Roth (Ger. P. 191914, of 1905) passes air through a porous medium into a mixture of 200 parts by weight of clay, 100 fine sand, 75 lime, 20 magnesia, 200 iron, and 600 water, heated to 60°. The specifically lighter nitrogen diffuses first through the medium and is retained in the form of NH_3 before the oxygen can act. When 10 mg. NH_3 has been formed for 1 litre of water, the formation of fresh NH_3 takes place much more slowly. But if now 1 per cent. ferric sulphate or ½ per cent. sulphuric acid is added, the mass again energetically forms NH_3. Thus after a few hours a cheap fertilizer is obtained, containing 6 per cent. N, which is dried, ground, and used without extracting the ammonia.

Jellinek (*Z. angew. Chem.*, lxxi., p. 121) discusses the function of iron as catalyzer for the synthesis of ammonia under pressure.

Matignon (Fr. P. 430595; B. P. 17411, 1910) employs for the synthesis of ammonia *palladium* or *zinc*, with or without the application of pressure. Zinc admits of working at lower temperatures. The U.S. Ps. are 1089240 and 1089241.

The Centralstelle für wissenschaftlich-technische Untersuchungen G. m. b. H. (Ger. P. 252997; U.S. P. 1119534, transferred to Dynamit A.G., Hamburg) produces ammonia from its elements by means of *ruthenium* or a ruthenium compound as catalyzer, whereby at 450° and under a pressure of only 80 atmospheres a reaction product containing 11 to 12 per cent. by volume of ammonia can be regularly obtained. The British patent was taken out by A. J. Boult, 14585, of 1912.

Lipski (*Z. Elektrochem.*, 1909, xv., p. 189) investigated the synthesis of ammonia from its elements by the mediation of *cerium nitride*. This compound dissociates at 600° to 700°, with a maximum tension of 34 to 40 cm. mercury. Probably metallic cerium forms with cerium nitride a solid solution, which causes the slow establishment of an equilibrium. No more convenient solvent for cerium nitride could be found. The reactions:

$$(a)\ 3H_2+CeN = CeH_3+NH_3$$
$$(b)\ N_2+CeH_3 = CeN+NH_3$$

go on smoothly at moderate temperatures in open vessels, without any sensible reaction according to the equation: $3H_2+2CeN = 2CeH_3+N_2$. Extremely small quantities of moisture or oxygen cause a superficial change of the cerium nitride and hydride, and make it useless for the formation of ammonia. If water and oxygen are completely excluded, both substances act as catalyzers for the synthesis of ammonia. After some time this action ceases, but is restored by repose. The most favourable temperature for the formation of ammonia is between 200° and 300°; the ammonia contents of the gas comes up to 1 per cent. by volume. It makes no difference whether the contact substance is made from pure or technical cerium.

Kunheim & Co. (Ger. P. 276986) produce ammonia from the elements with the acid of cerium nitride as catalyzer. That nitride is obtained by the action of nitrogen upon large pieces of cerium metal; mixtures containing at least 20 per cent. cerium nitride may be employed. In this process the pieces increase in size, and break up into many smaller pieces, so that nitride surfaces entirely free from oxide are obtained. The nitride can also be produced by saturating cerium metal with hydrogen, and replacing the hydrogen by nitrogen at a high temperature. In order to retain the catalytic effectiveness of the cerium nitride, the mixture of N and H must be carefully purified from oxidizing or other impurities. With this catalyzer, ammonia concentrations of 1·5 to 2 vol. per cent. can be obtained, with about 100 atmospheres' pressure and high gas speeds (*e.g.*, 60 litres per hour) for a contact-chamber of only 4 c.c. contents.

Hlawaty (Ger. Ps. 275343, 275663, and 277054) employs as catalyzer a mixture of *titanium* with one or more metals of the platinum group, precipitating them altogether on a suitable substratum. It is advisable to submit the gas mixture, before passing it over the catalyzer, to the action of an electric arc. The temperature should never exceed 500°. The pressure should be in turns raised or lowered, according to whether the gases are to be absorbed or driven out. According to his Ger. P. 283447 the most active contact mass for this process is a mixture of titanium and platinum in proportion to their atomic weights, *i.e.*, 48 parts by weight of titanium + 195·2 parts of platinum, especially at lower temperatures. By this mixture twice as much ammonia is obtained as by a mixture of equal parts of titanium and platinum.

Nicodem Caro (Ger. P. 272638) recommends as catalyzer for ammonia soda-lime or potassa-lime, impregnated with titanium or *vanadium*, or a mixture of these, because they are less sensitive to "contact poisons" than the metals of the iron group, so that technical hydrogen, produced by splitting up hydrocarbons, may be employed.

Various Catalyzers.—W. A. Phillips (B. P. 22046, 1911) and Brochet and Boiteau (Fr. P. 425952) combine N and H by the action of the metals of the alkalis and the alkaline earths.

F. Schreiber (*Chem. Zeit.*, 1911, p. 943) discusses the catalytical production of ammonia from nitrogen-carbon compounds.

Heckert (Ger. P. 288524) employs for this purpose the red-hot coke remaining in the retorts or chambers after carbonizing coal.

The Elektrochemische Werke G. m. b. H., Berlin (Ger. P. 238137), prepare ammonia or ammonium compounds from nitrogen oxides and hydrogen, or from mixtures of hydrogen with gases containing carbon monoxide or hydrocarbons, by passing them over various contact substances (Pt, Cu, Ni, Fe) at high temperatures, different for different contact substances.

Bucher (U.S. P. 1138190) fixes atmospheric nitrogen by bringing free nitrogen and sodium vapour into contact with a catalyzer, formed of iron, carbon, and sodium carbonate at a temperature of about 920° to 1000°, in order to form sodium cyanide, and supplying fresh carbon to the catalyzer as it is consumed by the reaction. Metallic sodium may be used to start the reaction or, indeed, sodium hydrate, acetate, bicarbonate, or oxalate may be used with an easily reducible iron compound on carbon. His U.S. P. 1138191 describes the fixation of free nitrogen by bringing it into contact with sodium carbonate, and a catalyzer formed of a finely powdered mixture of iron and graphite at a temperature of about 725°, to form sodium cyanide. The latter may be acted on with steam, as formed, to produce ammonia. Other patents of the same inventor for preparing sodium cyanide from atmospheric nitrogen are U.S. Ps. 1091425, 1116559, 1120682.

G. Calvert (B. P. 10612, of 1914) causes nitrogen and hydrogen to unite under pressure in the presence of a heated catalyzer, action being promoted by moving the catalyzer or heater, or both, relatively to the gases. For example, the catalyzer may be carried by a rotating arm, fitted with a heating coil, which is driven by an electric motor contained in a chamber communicating with the reaction chamber, as described in B. P. 18350, of 1913 (Fr. P. 468426).

The Farbenfabriken vorm. Bayer (Ger. Ps. 285698 and 286719) combine nitrogen and hydrogen by means of catalyzers, obtained by heating alkaline or earth-alkaline ferrocyanides with exclusion of the air up to decomposition, preferably below 500°; *e.g.*, barium ferrocyanide in a high-pressure apparatus at 430° under a pressure of 180 atmospheres.

F. W. de Jahn, Assignor to the General Chemical Co. of New York (U.S. P. 1141948), passes mixture of nitrogen and hydrogen under a pressure of less than 100 atmospheres over a heated catalyzer, containing cobalt, sodium, and nitrogen. Other catalyzers for this purpose are described in his U.S. Ps. 1151537, 1159364, 1159365.

The same (U.S. P. 1143366) prepares a catalyzer suitable for use in the synthesis of ammonia by reducing nickel oxide with hydrogen, adding metallic sodium, and treating the product with ammonia.

Matignon (U.S. P. 1089241) employs *tungsten* as a catalyzer.

H. Wade (B. P. 213, of 1914; communication from Dr M. Pier) employs a catalyzer composed of *iridium* or *rhodium*, or their compounds, in conjunction with a basic contact-carrier, such as an alkaline or earth-alkaline oxide or carbonate, or chromic oxide.

According to M. Pier (U.S. P. 1119534), *ruthenium* and its compounds, especially potassium rutheniate, K_2RuO_4,H_2O, perrutheniate, $KRuO_4,H_2O$, and the hydrate, $RuO(OH)_3$, have a prominent action as catalyzers for the combination of N and H to NH_3, considerably exceeding that of osmium. At 450° and a pressure of 80 atmospheres, a gas containing 11 to 12 vol. per cent. NH_3 is obtained, and at a pressure of 175 atmospheres the percentage rises up to 20 per cent. According to his B. P. 214, of 1914 (communicated to H. Wade), catalyzers consisting of ruthenium chloride or iridium chloride, with or without metals of the platinum group, or iron, cobalt, nickel, molybdenum, tungsten, or uranium, or compounds of these metals, may be employed on a carrier of magnesium oxide or carbonate, whose quantity is a multiple of that of the catalytic agent. His U.S. P. 1157253 (B. P. of Wade, No. 213, 1914) describes an alkaline carrier.

Koppers (Ger. P. 285354) describes an apparatus for carrying out his process (Ger. P. 257188) for preparing ammonia from nitrogen-containing carbon compounds, in the shape of ammonium sulphate.

Anderson (Ger. P. 277222) describes metallic vessels for contact reactions.

Synthesis of Ammonia from Nitrogen and Hydrogen by the Aid of the Electric Current.

Ammonia is formed by the direct combination of nitrogen and hydrogen under the mediation of the electric current.

This takes place both by the induction spark (Regnault, Deville, etc.), and by the dark electric discharge (Donkin, *Roy. Soc. Proc.*, lxxxi., p. 281). Numerous attempts have been made at utilizing this reaction for technical purposes, of which we mention in this place only those where H and N are directly united; the cases where intermediary compounds, nitrides, are formed, will be treated hereafter.

Young (B. P. 1700, of 1880) passes electric sparks through a mixture of 3 vols. H + 1 vol. N.

W. Müller and E. Geisenberger (Ger. P. 11489) employ combustion gases, which are freed from carbon dioxide by means of lime, as a source of nitrogen. Hydrogen is to be obtained by the action of steam on red-hot coke. The mixed gases are to be united by the electric spark. Another proposal of the same inventor (Ger. P. 12364) is: passing the gases obtained by heating alkaline nitrates, together with steam, over red-hot coal. The alkaline residue is to be reconverted into the original salts by the joint action of oxygen, nitrogen, and the electric current.

The Société l'Azote (Ger. P. 17070) aims at combining the nitrogen of air with the hydrogen of water by the action of porous substances and of electricity. Melted zinc is run into two furnaces kept at a red-heat; into one of them is passed air, and water into the other. In both cases zinc oxide is formed; and there is liberated nitrogen on one side, hydrogen on the other. The gases are passed through dust-chambers to deposit zinc oxide, and thence through retorts containing titaniferous iron-sponge. Here the nitrogen is first absorbed, and is then converted into ammonia by hydrogen. The formation of ammonia is promoted by employing in the retorts a mixture of iron with other metals, whereby an electric current is said to be produced. They also employ platinized coal into which is forced first nitrogen, then hydrogen, at a pressure of 10 atmospheres.

Nithack (Ger. P. 95532) produces ammonia by saturating water under high pressure with gaseous nitrogen, passing an electric current through this, and continuing to introduce nitrogen under the same pressure. He asserts that the nitrogen is quantitatively transformed into ammonia, and that solutions of commercial strength are quickly formed

At the positive pole ammonium nitrate is formed. His process is carried out as shown in Fig. 229. The cylinder G contains at the bottom sieves, S, for dividing the gas; at the top the non-conducting electrical portion, E. A number of carbon rods, K, connected by the metallic conductors, *m*, form the hydrogen pole, a platinum wire-gauze cylinder, *p*, the oxygen pole; they are separated by the porous diaphragm, *d*, tightly fitting on the annular bottom, *a*, of part E. Just below the level of the liquid, *d* is connected with a porcelain vessel, *i*, reaching to the top of G and preventing any mixture of oxygen and hydrogen. The apparatus D indicates any difference of

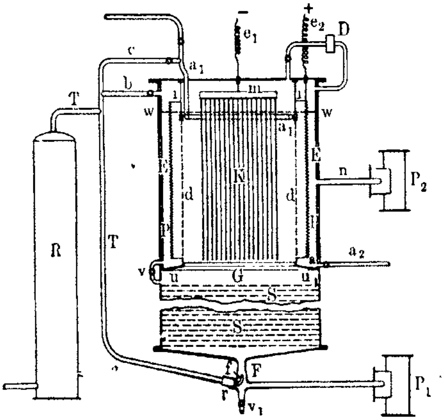

Fig. 229.

pressure between the two chambers thus formed and remedies this at the same time. The ammonia liquor runs off through the perforated pipe a_1; the liquid formed at the oxygen pole passes through pipe a_2. *c* serves for introducing nitrogen, *b* for increasing the pressure, *v* for communication between the two electrode chambers; R is the washer, connected with the air-pump supplying the nitrogen. The process is carried on in the following way:—After G has been filled with water, first low-pressure air, freed in the washer R from oxygen and CO_2, is passed through T *r f* or T *c* a_1 into G, the water running off through F and valve v_1 to the level of the sieves S. Now v_1, *b*, and *c* are closed, and by means of a high-pressure pump nitrogen is forced in through R T *r* and *f* at 50 to 100 atmospheres' pressure, at the same time as water runs through pump P_1. As soon as the liquid has risen to *n*, the pole wires, e_1 and e_2, are connected with the source of electricity. At K the nascent hydrogen forms with the nitrogen ammonia, which dissolves in the water and is carried off through a_1. At *p* at first only oxygen is formed and let out at D. Later on ammonia diffuses through the diaphragm *d* and is oxidized to ammonium nitrate; if sufficient ammonia does not diffuse to fix all the oxygen, more is pumped in through *n* by means of pump P_2.

Briner and Mettler (*Comptes rend.*, 1907, cxliv., p. 694), when sparking a mixture of N and H at ordinary temperatures, produced only 3 to 4 per cent. NH_3, but at the temperature of liquid air almost complete combination was effected. The maximum production occurred at a pressure of about 100 mm., when 0·17 g. NH_3 was produced per kilowatt hour.

The West-Deutsche Thomasphosphatwerke (Ger. Ps. 157287 and 179300) make NH_3 from a mixture of hydrogen, nitrogen, and carbon monoxide by the dark electric discharge, carrying off the heat of reaction (which reduces the yield in consequence of the formation of ammonium formiate) by cooling-arrangements, so that the temperature never exceeds 80° C., and is preferably kept at 65° C. In this case about 20 per cent. of the nitrogen can be converted into ammonia. The above mixture is most cheaply obtained in the shape of "mixed gas," by blowing air and steam into a gas-producer fed with coke.

Goriainoff (Fr. P. 368585) electrolyzes water, employing part of the hydrogen formed to prepare pure nitrogen from air by taking out the oxygen, and combining this nitrogen with another part of the hydrogen to form ammonia by means of electric discharges, or else with the electrolytic oxygen to form nitric acid.

Hooper (U.S. P. 791194) employs the electric current in this way: the cathode cell is filled with a solution of ammonium sulphate, the anode cell with a solution of sodium chloride; the temperature is kept at 100° C. At the cathode NH_3 and H escape, at the anode Cl. This is united with the H to HCl, after taking the NH_3 out of the gaseous mixture.

Cassel (Ger. P. 175480) gets NH_3 by electrolysis of nitrates or nitrites, with addition of a small quantity of a soluble lead salt. The nitrates or nitrites are obtained from atmospheric air by the electric current.

Herford (U.S. P. 940972) produces ammonia from mixtures of 1 vol. nitrogen and 3 vols. hydrogen by electric discharges; the ammonia formed thereby is immediately combined with sulphuric acid blown in, and the solution of ammonium sulphate is run off.

Blackmore (U.S. Ps. 979633, 974741, 974742) obtains ammonia by agitating a mixture of nitrogen and hydrogen with sand or mercury, previously impregnated with calcium or palladium, by heating or by passing an electric current through it. A continuously changing pressure may also be employed.

Summers (U.S. P. 1125208) heats nitrogen in an electric arc and then mixes it with hydrogen (or, for the production of nitrogen oxides, with oxygen), and immediately withdraws the products to a cooled zone, for which purpose apparatus is described.

Classen (Fr. P. 470916; Ital. P. 141275) submits mixtures of nitrogen with hydrogen (for the production of nitrogen oxides, with oxygen) to the silent electric discharge between 25° and 100° in the presence of contact materials (colloidal metals or alloys), for which purpose he describes a tubular apparatus.

Lepsius (Fr. P. 466102) passes the mixture of NH_3, N, and H, coming out of the contact chamber, into the cylinder of a compression engine, where it does work and is cooled by expansion; on leaving the engine it goes into the absorbing-apparatus, and the gases coming out of this are compressed, whereby they get heated.

Le Blanc (*Chem. Zentr.*, 1914, ii., p. 117) found that in the formation of ammonia from the elements by silent electric discharges the law of the action of masses is not valid. The rate of formation depends on the dimensions of the apparatus, on the density of the current, on the frequency of the oscillation of currents, etc. This agrees with a former investigation of Leblanc and Davis (*Chem. Zentr.*, 1908, ii., p. 377).

Winstanley and Williams (B. P. 21304, of 1912) distil nitrogenous matter, such as waste from wool, hair, leather, etc., in a retort in contact with hydrogen, produced by passing steam over red-hot iron, and at the same time pass an electric current of say 12 amps. and 150 volts through the retort, returning the issuing gases into the retort until they are sufficiently rich in ammonia; the residue of the distillation is utilized as animal charcoal.

Production of Ammonia from Free Nitrogen by the Intervention of Nitrides.

By Boron Nitride.—N. Basset (B. P. 4338, 1879) heats coal impregnated with boric acid, and covered with a layer of magnesia, lime, oxide of manganese, etc., in a retort, and passes nitrogen over the mixture. When a sufficient quantity of boron nitride has been formed, steam is introduced, and the ammonia now obtained is carried away.

G N. Tucker (Ger. P. 13392) mixes carbon, impregnated with borates, with alkaline carbonates, or the oxides of manganese, antimony, iron, titaniferous iron, or with the borates of these metals. These are exposed to a red-heat in retorts; gas rich in nitrogen is passed in, so that the nitrogen combines with boron; then steam is passed in, which is decomposed by the carbon or the metal, and supplies the hydrogen necessary to form ammonia. Or else air or nitrogen and steam are mixed before introducing into the retort, in the proportion of 3 vols. HO_2 to 1 vol. N. The borates and the metallic oxides contained in the residue are to be used over again. The gas is purified by milk of lime from carbonic acid, hydrogen, sulphide, and tarry substances.

Lyons and Broadwell (U.S. P. 816928) pass nitrogen or gases containing such into a bath consisting of fused borates of the positive metals, kept at about 1000° C. At the cathode, boron nitride is formed, which is afterwards transformed by means of steam, at a temperature of 600° or upwards, into boric acid and ammonia:—

$$2BN + 3H_2O = B_2O_3 + 2NH_3.$$

Mond (*J. Soc. Chem. Ind.*, 1889, p. 815) believes that boron nitride cannot be utilized for the purpose in question, owing to the high temperature required for its formation, and the volatility of boric acid with steam.

The Comp. franç. pour l'exploit. des prod. Thomson-Houston (Fr. P. 377683, addition No. 17669; 456488) obtains boron nitride by heating boric anhydride with cyanides or ferrocyanides in an electrical furnace to 2000°.

Heyden and the General Electric Co. (U.S. P. 1077712) heat a mixture of boric acid, magnesia, and ammonium chloride in a muffle to 800°, and obtain from the product boron nitride by washing with dilute sulphuric acid and drying *in vacuo*. Staehler (Ger. P. appl. S18025) also uses boron nitride.

The preparation of pure or nearly pure boron nitride from boron compounds, *e.g.* trioxide, by means of ammonia, is described in the Ger. P. 282701 of Ehrich and Graetz.

Podszus (Ger. P. 282748) prepares solid lumps of boron or titanium nitride by moulding the oxides into pieces, heating these up to the sintering point, and converting them into nitrides by heating in an atmosphere of ammonia. These nitrides dissociate only above 2000°, and are the best of all materials for the construction of furnace linings and crucibles.

By Silicon Nitride.—L. Roth (Ger. P. 197393) employs silicon carbide for preparing silicon nitride. He prescribes avoiding the injurious action of the atmospheric oxygen in preparing the nitrides from air, by dialyzing the air by means of a finely powdered mixture of amorphous silicon carbide (which is obtained as a by-product in the manufacture of carborundum), with half its weight of iron. This mixture is spread on slabs of burnt clay, 2½ in. thick, which are placed in a furnace. If air is passed through this, the nitrogen diffuses first, and can be converted into nitrides (*cf.* his Ger. P. 191914 *supra*, p. 1086).

Sinding-Larsen and Storm (Ger. P. 217037) prepare silicon nitride from silicon in the shape of a metallic alloy, liquid at the temperature of reaction, by treating it with nitrogen. The other constituent of the alloy subjected to this treatment is distilled into a receiver. Silicon at high temperatures easily combines with nitrogen, but a quantitative conversion into nitride is prevented by the fact that the nitride formed at first forms a coating on the silicon still present as such. This is avoided by dissolving the silicon in a metal with which it forms a mass liquid at the temperature of reaction, *e.g.* iron or aluminium. From this alloy by means of a current of nitrogen at a suitable temperature all the silicon may be obtained as nitride, and that in such a state of fine division that it may be immediately applied as a fertilizer, or for the preparation of other compounds. Another patent of the same inventors (Ger. P. 229638) prescribes attaching the treatment with nitrogen immediately to the preparation of the silicon, by vaporizing this in the moment of being liberated and bringing it together, outside the mass from which it has been formed, with nitrogen heated to a sufficiently high temperature.

Weiss and Engelhardt (*Z. anorg. Chem.*, lxv., p. 38) made a laboratory investigation of the nitrogen compounds of silicon. By heating pure silicon in a current of nitrogen at a temperature of 1300° to 1400°, they prepared three different nitrides, viz., Si_2N_3 and SiN by heating for an hour, one or the other of the just-named nitrides being obtained according to subsequent purifying processes; by prolonging the treatment up to a complete saturation with nitrogen, the proper silicon nitride Si_3N_4 is formed. These nitrides show a great resistance to chemical influences.

Serpek (Fr. P. 433925) also describes the preparation of silicon nitride.

The Badische Anilin- und Sodafabrik (Fr. P. 405712; Ger. Ps. 234129 and 241510) states that silicon nitrides can be easily and at comparatively low temperatures prepared by treating mixtures of silica and carbon, in the presence of metals or metallic compounds, with nitrogen or gaseous mixtures containing nitrogen. *E.g.*, a mixture of 70 kg. quartz, 5 kg. iron, and 25 kg. soot is heated during twelve hours to 1400° in a current of nitrogen. Or else masses containing silica are employed, especially silicates containing to begin with such metals or metallic compounds, like river gravel, kaolin, or granite, which at 1500° and above this furnish abundantly nitrogen compounds. In such cases where the metals or metallic compounds present are capable of forming nitrides as well, the product is of course a mixture of silicon nitride with metallic nitrides. From the nitrogen compounds obtained in this way, ammonia can be prepared by treating them with basic oxides, hydroxides, or salts in the presence of water, *e.g.*, by heating the product with milk of lime in an autoclave to 160°.

By Titanium Nitride.—Tessié du Motay allowed a mixture of nitrogen and hydrogen to act upon titanium nitride. Titanium forms two nitrides, the higher of which is at high temperatures reduced by hydrogen to the lower, with formation of ammonia. When passing a mixture of hydrogen and nitrogen over the higher titanium nitride, Mond never obtained so much ammonia as would be formed without any free nitrogen. Hence the lower nitride does not combine with more nitrogen, which according to him makes the process impossible.

Huntington (*Eng. and Min. J.*, 1892, p. 607) obtained from titanium nitride, prepared from titanium and nitrogen, only traces of ammonia by means of hydrogen.

The Badische Anilin- und Sodafabrik has given great attention to the preparation of ammonia by the mediation of titanium nitrides. According to the U.S. P. 957842 (taken out by Bosch and assigned to the Badische), titanium nitrides are prepared by heating a mixture of 80 parts titanic acid, 20 charcoal, and 2 sodium sulphate in the presence of nitrogen at temperatures above 1100°, preferably at 1240°, whereby Ti_2N_2 or another nitride or cyanamide is formed. The same firm (U.S. P. 957843) prepares ammonia or its salts by heating titanium nitride with air in the presence of caustic soda and cupric oxide, or sulphuric acid, or calcium chloride, or sodium bisulphate, or ferric sulphate and water. The reaction is facilitated by adding oxides of iron, manganese, mercury, cerium, or alkaline carbonates.

Their Ger. P. 203750 also protects the addition of alkali salts (sulphates or carbonates) for the purpose of accelerating the reaction. Already when adding only 2 parts sodium sulphate to 80 titanic acid and 20 charcoal, the nitride is quickly formed at temperatures of about 1240°.

Their Ger. P. 200986 describes the preparation of the cyanides of the alkalies and alkaline earths from titanium nitrides and cyanonitrides. The titanium nitride is heated with the oxides, carbonates, sulphates, etc., in the presence of carbon or of compounds containing this, with or without fluxes. The alkalis yield only cyanides, baryta, a mixture of cyanide and cyanamide, lime almost entirely calcium cyanamide. The titanic acid can be recovered from the melt. Ammonia is obtained from the titanium cyanonitride in many ways.

Their Ger. P. 202563 describes the working with oxidizing agents, avoiding temperatures of such height that the ammonia would be converted into nitrogen. Suitable oxidizing agents are chromic acid, manganese peroxide, ferric oxide, mercuric oxide or their salts; sulphuric acid or bisulphates; electrolysis in the presence of oxygen carriers; or air in the presence of water or steam at high pressure in the presence of acid and iron salts.

Their Ger. P. 203748 states that when proceeding according to 202563, in lieu of ammonia, or along with this, nitrogen oxides are obtained, if the treatment of the titanium cyanogen-nitride with oxidizing agents (*e.g.*, a current of air and steam at 300° to 400°) is carried out in the presence of a contact substance, *e.g.*, a very dilute solution of platinum.

Their Ger. P. 204204 shows that other nitrides of titanium may be treated as shown in Ps. 202563 and 203748. P. 204475 states that as oxidizing agent steam may be employed in the presence of some compounds (sodium carbonate, sodium hydrate, calcium chloride), which by themselves do not oxidize titanium nitrides. This has the advantage that the temperature of the reaction may be lowered to 300° to 500°, which prevents the destruction of the ammonia formed.

According to their Ger. P. 204487 ammonia may be prepared from titanium nitrides by heating them with acids or salts, splitting off acids under such conditions that no oxidation can take place; *e.g.*, with concentrated sulphuric acid at 150°, whereby a lower degree of oxidation of titanium goes into solution, or by boiling with sulphuric acid of 30 per cent. with exclusion of air, or by heating with hydrochloric acid to 200° under pressure.

Patents of the Badische for preparing and working up titanium nitrides in other countries are:

B. Ps. 1841, 1842, 2414, of 1908; 2525, of 1909.

Fr. Ps. 387001, 387002.

U.S. P. 923012.

Landmark (Norw. P. 20198, of 1909) prepares ammonia by heating titanium nitride with coal and steam, according to the reaction:

$$2TiN_2 + 3C + 3H_2O = 2TiN + 2CO + 2NH_3.$$

The TiN formed is easily brought back again to TiN_2 by treating it with nitrogen. The process may be carried out continuously by passing a mixture of nitrogen and steam over a mixture of titanium nitride and coal. The evolution of NH_3 goes on until all the coal has been consumed; the CO formed from it may be utilized for heating the apparatus.

Bronnert (report to the *Bull. Soc. Ind. Mulhouse*, 1909, p. 39) states that he never succeeded combining more than 12 per cent. nitrogen with titanium in the shape of nitride.

Ruff and Treidel (*Berl. Ber.*, 1912, p. 1364) report on their investigations of titanium nitrides. Apart from the "Titanstickstoff," prepared already by Wohler (who gave it the formula Ti_3N_4, which, however, has been recognized by Ruff and Eisner, *ibid.*, 1908, p. 2250; 1909, p. 900, as having a composition according to the formula TiN), which they call "titan*o*nitride," they succeeded in preparing "titan*i*nitride," Ti_3N_4, which, otherwise than TiN, is decomposed by water into hydrated titanium dioxide and NH_3, and which on heating to comparatively low temperatures is split up into $3TiN + N$. This fact induced them to try the possibility of obtaining ammonia by the action of nitrogen and hydrogen in the proportion of $N_2 : 3H_2$ on the potassium salt of titanium di-imide, Ti (NH) NK. At 360° a contraction of the gaseous mixture could be observed which led them to conclude that ammonia had been formed.

Sinding-Larsen and Storm (Norw. P. 24423) obtain titanium nitride by treating titanium oxide with chlorine or sulphur in the presence of reducing substances, and then allowing nitrogen to act on the product at a higher temperature.

By Magnesium Nitride.—Willson (B. P. 21755, of 1895) prepares magnesium nitride by passing nitrogen through a mixture of magnesia and carbon heated in an electric furnace, and decomposes it by steam into ammonia and re-formed magnesia. The nitrogen is obtained from atmospheric air, which is deprived of its oxygen by red-hot coke, which is thus converted into CO; or preferably by blowing the furnace for CO_2 and fixing this by lime, so that pure nitrogen is obtained. [A very just critique of this patent is given in *Z. Elektrochem.*, 1896, p. 274.]

Rossel and Franck (*Chem. Zeit.*, 1896, p. 38) also propose to employ magnesium nitride, but they prepare this in a most impracticable and costly way, by heating calcium carbide with metallic magnesium in the presence of air.

Borchers and Beck (Ger. P. 196323, of 1908) prepare nitrides of metals from atmospheric nitrogen by the assistance of the electric current in a similar way, as is employed in the electrolysis of alkaline chlorides, where the cathodic mercury is charged with alkaline metal, which is taken out of it, so that the mercury can be used over again. An alloy of *tin and magnesium*, electrolytically formed, is by the action of nitrogen in another space partially converted into magnesium nitride; the alloy, now containing much less Mg, returns to the cathode space to be again enriched with Mg. The magnesium nitride is converted into ammonia by means of water or of steam, and the process may be conducted in such manner that anhydrous ammonia and anhydrous MgO are formed. The latter is used over again in the electrolytic cell.

Another process for that purpose is that of Roth (Ger. P. 197393).

Matignon and Lassieur (*Comptes rend.*, 1912, p. 63) show that by heating magnesium powder with air at 600° and upwards, very little N is absorbed, nearly all the Mg passing over into MgO. According to the same authors (*Bull. Soc. Chim.*, 1912, p. 262), magnesium nitride is obtained by heating magnesium in a crucible almost completely closed and placed in a muffle at such a temperature that it volatilizes. The magnesium vapour combines slowly with the nitrogen of the air, forming crystalline nitride.

Wallace and Wassmer (B. P. 18450, of 1912; U.S. P. 1083232; Fr. P. 464692) convert magnesium into nitride and divide this into two portions, one of which is treated with hydrogen sulphide to convert it into magnesium sulphide, and the other with hydrochloric acid to form chloride. The sulphide and chloride are then electrolyzed together, and the metal obtained is again converted into nitride, and so on; the S and Cl and the chlorides of sulphur also produced by electrolysis being treated to form H_2S and HCl. Chloride may also be introduced from an outside source and only part of the metal converted into nitride.

J. E. Bucher (U.S. Ps. 1113598 and 1113599, assigned to Nitrogen Products Co.) fixes nitrogen by magnesium, prepared by electrolysis from magnesium chloride, converts the chlorine liberated at the same time into HCl, and uses this to react on the magnesium nitride, to form NH_3 or NH_4Cl, and regenerate the $MgCl_2$. Or else he treats the magnesium nitride with water to form NH_3 and MgO.

By Calcium Nitride.—Kaiser (B. P. 26803, 1905; Ger. P. 181657; Fr. P. 350966) obtains NH_3 by heating calcium nitride in a current of hydrogen under high pressure; the calcium is reduced to the metallic state, or to a hydride when the hydrogen is in excess. If now nitrogen is passed over it, calcium nitride is re-formed. A continuous production of NH_3 can be effected by heating metallic calcium alternately in a current of nitrogen and hydrogen. This takes place all the more readily when the metal is deposited on asbestos in a finely divided state. The reaction sets in at about 150° C.; the best results are obtained between 200° to 400°. The velocity of the current of gases is regulated by observing whether on exceeding a certain velocity the transformation into ammonia is no more complete. Good results are obtained by passing 20 to 30 litres of gas and upwards per hour through the catalyzer.

Collet and Eckardt (Norw. Pat. 19716) also employ calcium nitride for this purpose. So does Peacock (U.S. P. 1147184).

Lidholm (Ger. P. 277525) obtains a technically complete yield of ammonia, from calcium nitride by heating with water under pressure in the presence of alkaline hydroxides or carbonates.

By Aluminium Nitride.—A great deal of attention has been given to the synthesis of ammonia by means of aluminium nitride, principally in connection with the results obtained by Serpek.

Serpek (Ger. Ps. 181991 and 183702) in the year 1905 obtained aluminium nitride by allowing nitrogen to act in an electric furnace on a mixture of 4 parts alumina, 2 parts carbon, and 0·5 part copper, moulded into bricks. Very soon a strong evolution of carbon monoxide sets it, whereupon nitrogen is admitted. It is best to allow the nitrogen to act upon a mixture of alumina and calcium carbide; thereby a product containing up to 17 per cent. nitrogen is obtained, so that the reaction must be nearly quantitative. The absorption of nitrogen is hastened by the addition of a little calcium chloride. From the nitrides formed the ammonia is obtained in the usual way.

On this process Bronnert (*Bull. Soc. Ind. Mulhouse*, 1909, p. 39) reported as follows:—Serpek was the first to carry out the industrial preparation of aluminium carbide by heating a mixture of aluminium oxide and carbon in an electric furnace, in the shape of large, yellow crystals. This carbide behaves otherwise than calcium or barium carbide; in contact with water it does not give off acetylene, but methane. If it is heated and treated with pure nitrogen, no cyanide is formed (as observed by Frank and Caro in the case of calcium carbide), nor a mixture of cyanide and cyanamide (as found by Frank, Caro, and Roth in the case of barium carbide), nor cyanamide by itself (found by Frank, Pfleger, and Caro when working with pure calcium carbide), but aluminium nitride, Al_2N_2. This compound is not isolated, but immediately more alumina is added and nitrogen passed in, whereby mixtures containing from 20 to 24 per cent. nitrogen are obtained, which may be employed as such for fertilizing purposes, since under the influence of water and atmospheric oxygen they gradually give off ammonia. In an experimental factory at Mulhouse-Niedermorschweiler, from this compound crystallized aluminium nitride, AlN, with 34 per cent. nitrogen, was obtained. The action of nitrogen on aluminium carbide takes place at comparatively low temperatures; as a source of nitrogen, producer-gas may be employed which, along with 77 per cent. nitrogen, contains only CO and a little CO_2. [This statement is contradicted by Keler in *Z. angew. Chem.*, 1909, p. 1445, who states that the Serpek process must be carried out with pure nitrogen.] The consumption of electric energy for the fixation of nitrogen in the shape of AlN is only half as large as that for producing cyanamide, and only an eighth of the amount required for the combustion of nitrogen to nitric acid by the process of Birkeland and Eyde. [*Cf.* Lunge's *Sulphuric Acid and Alkali*, 4th ed., vol. i., pp. 232 *et seq.*, 1913.]

According to a further patent of Serpek's (Ger. P. 216746, of 1908), a mixture of alumina and carbon is placed in an electrically heated furnace upon liquid ferric carbide, with a strong supply of nitrogen or producer-gas rich in nitrogen, and the aluminium nitride formed is drawn out at the other end of the furnace. Thus in a continuous way a carbide is obtained which at once reacts with more alumina, with formation of metallic aluminium, which alloys itself with the metallic iron formed at the same time, and immediately combines with nitrogen, forming an aluminium nitride containing an unprecedentedly high percentage of nitrogen. The reaction is:

$$Al_2O_3 + Al_4C_3 = 6Al + 3CO \text{ and } 6Al + 6N = 3Al_2N_2.$$

The carbon monoxide formed is collected and employed for drying and pre-heating the mixture of alumina and carbon.

Another process of Serpek's (Ger. P. appl. S27492) consists of heating a mixture of alumina and carbon until 15 to 20 per cent. of it has been transformed into carbide. Avoiding this to be fused, nitrogen is passed in, whereupon immediately nitride is formed, with development of much heat and formation of CO.

According to Serpek's B. P. 7507, of 1909, alumina or alumina compounds, mixed with carbon, are heated in an atmosphere of nitrogen not over 2000°, whereby nearly pure aluminium nitride with an average content of 30 per cent. nitrogen is obtained.

The preparation of ammonia from the aluminium nitride, according to Serpek's B. P. 15997, of 1909, is effected by boiling the latter with a solution of potassium aluminate. The nitride resists pretty well the action of pure water, even at temperatures above 100°, but by potassium aluminate the decomposition takes place completely and sufficiently quickly. A solution of potassium hydrate is added to the nitride and boiled, whereupon aluminate is formed and ammonia is given off in large quantities. The solution of aluminate thus obtained is employed for decomposing further quantities of nitride. Within one to one and a half hours, all the nitrogen of the nitride is obtained in the shape of NH_3. For 100 parts of aluminium nitride there is employed 120 parts of potassium aluminate and 200 parts water.

The B. Ps. 12601 and 16522, of 1909, and 13086 of 1910 describe improvements in the revolving furnaces employed for Serpek's processes.

The following notes on aluminium nitride and the preparation of ammonia from it I owe to a direct communication rom Dr O. Serpek. If aluminium powder in the shape of "bronze" is treated with nitrogen at temperatures from 650° to 700°, the N is absorbed by the Al, with considerable evolution of heat, and aluminium nitride of the formula Al_2N_2 is produced. By employing pure "aluminium bronze," perfectly pure nitride is obtained. This method is, however, too expensive for working on the large scale, on account of the high price of aluminium metal. But the more easily and cheaply obtained aluminium carbide, Al_4C_3, may be employed for manufacturing the nitride. As stated in Serpek's Ger. Ps. 181991, 181992, 183702, 235669, technical aluminium carbide at 1100° to 1200° takes up nitrogen, nitride being formed. The yield is greatly raised by mixing alumina with the carbide. In fact it is not the carbide itself which fixes the nitrogen, but the reaction is:

$$Al_4C_3 + Al_2O_3 + 6N = 3CO + 6AlN.$$

To be sure, the carbide as well furnishes nitride, but only at the temperature of its dissociation. Since this method requires the previous manufacture of aluminium carbide, Serpek (as proved by his later patents) strove at finding a direct way of producing the nitride. His Ger. P. 231886 describes treating mixtures of alumina and carbon in the electric arc under special working conditions. In his Ger. P. 216746 he employs the same mixture in an induction furnace, under such conditions that in the first instance aluminium carbide is formed, which immediately reacts with alumina according to the just given equation. This process worked very satisfactorily for a long time, until Serpek succeeded in carrying out the production of nitride without the intermediate formation of carbide. This new process is described in Ger. P. 224628. It states that the reaction:

$$Al_2O_3 + 3C + 2N = 2AlN + 3CO$$

can be carried through at such temperatures that no carbide is formed, nor alumina is fused, and in the absence of nitrogen no reduction of the alumina takes place. At 165° the reaction is already so strong that a complete formation of nitride takes place within a short time. By the addition of small quantities of other substances the temperature of the reaction is considerably lowered; therefore the reaction goes on much more quickly when working with bauxite instead of with pure alumina. Here in fact the mass may be heated without the electric current; the temperatures obtained in tolerably well-constructed gas furnaces suffice for converting bauxite into nitride.

The process described in that patent is already in practical operation in Savoy, in a very simple manner. Bauxite is charged into an inclined revolving furnace, Fig. 230, similar to those used in the manufacture of Portland cement. The preliminary heating of the bauxite is effected in the upper cylinder, *a*, by the combustion of the carbon monoxide given off in *b*. The red-hot bauxite falls into the lower cylinder, *b*, in which a length of 5 metres is heated to 1500° by electric carbon-resistances. In this case the electric heating was preferred to heating by gas, in order to carry out the reaction in an atmosphere as free as possible from CO_2 and O. The nitrogen is supplied by producer-gas, containing about 20 per cent. CO, made in the producer *t*, and carried through *i* and *g* in an opposite direction to the solid mass; it is preheated by the nitride coming from the zone of reaction, in which it gives up its nitrogen and takes up the CO formed in the reaction. The gases, containing about 70 per cent. CO, are burned in the upper furnace, *a*, by atmospheric air, so that the bauxite is easily preheated there to 1600°. The carbon required for mixing with it is introduced in the vertical channel, *c*, connecting the furnaces *a* and *b*; this is done in order to

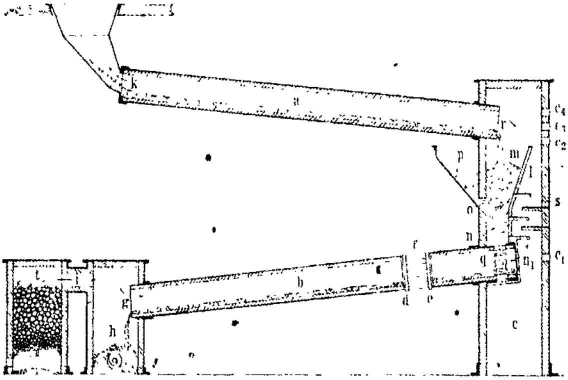

FIG. 230.

protect it from oxidation in *a* by the atmospheric air. The nitride is continuously discharged at *h* by means of a mechanical arrangement; it has a grey-white colour and the form of coarse powder, and contains from 24 to 32 per cent. nitrogen, varying with the quality of the bauxite employed.

It is remarkable that even from the white, silicious bauxites nitrides are formed, containing more nitrogen than corresponds to their alumina contents. This is explained by Serpek, in a further patent (Ger. P. 241339 of the Soc. Gén. des Nitrures), by the fact that silica in the presence of carbon and nitrogen volatilizes at 1400° in the shape of a compound containing carbon and about 5 per cent. nitrogen, and is carried away by the gases passing away from the furnace. The formation of this compound is the reason why silicium nitride cannot be produced on a large scale. If the heating is not carried up to 1300°, there is no volatilization, but the reaction between silica, carbon, and nitrogen requires several days; if the attempt is made to accelerate the process by raising the temperature, the volatilization sets in as just described.

The only impurity remaining in the aluminium nitride is metallic iron, from the bauxite, which may be easily removed in a magnetic way, but which causes no trouble when working the nitride for alumina and ammonia by Bayer's process (*Chem. Zeit.*, 1888, p. 1391, and 1893, p 39), as modified by Serpek.

The *working of the nitride for ammonia* is very simple. At ordinary pressures even boiling water does not act very easily upon nitride, but under a pressure of 4 to 6 atmospheres it is completely decomposed within two or three hours. The decomposition goes on much more quickly if the nitride is acted upon by alkaline leys, *i.e.*, applying the Bayer process, worked out for bauxite, to nitride. In the latter case the leys may be much weaker, and need not be concentrated again after distilling off the ammonia and precipitating the alumina; for by the reaction $2AlN + 3H_2O = Al_2O_3 + 2NH_3$ water is consumed, and thereby the alkaline ley is concentrated, and even more than indicated by that reaction, since aluminium hydroxide is also formed. Moreover, together with the ammonia, there is also a certain quantity of water evaporated. The washing-water from the precipitation of alumina mostly hardly suffices for imparting to the aluminate liquor, going back to the decomposing process the necessary degree of dilution. There is therefore no loss of alkali in this process.

His Ger. P. 272674 prescribes treating the aluminium nitride by a small quantity of solution of alkaline aluminate.

The production of *pure alumina* via the nitride is so cheap that all the aluminium factories belonging to the French Aluminium Syndicate have acquired the process, and at the time of reporting were busy with erecting the necessary plant

On the *properties of aluminium nitride* Serpek makes the following statements:—The nitride obtained from aluminium powder is amorphous, and not very easily acted upon by water. The nitrides prepared from mixtures of alumina and carbon are crystallized; the crystals are all the better formed, the higher the temperature in their production. Especially the crystallized nitride is a very stable substance. Even at 2500 it does not fuse, but only begins to dissociate. It is an excellent insulator for heat, and even at 1400° also for electricity. On account of its infusibility, the nitride is employed as lining in the furnaces serving for its production, which imparts to them an almost unlimited durability. By the atmospheric oxygen the nitride is not acted upon even at 1300°, and only above that temperature the nitrogen is gradually replaced by oxygen. Steam has also no action on it at high temperatures. It resists all acids, and is only slowly decomposed by hydrofluoric acid. Pure nitride is white like sugar; the crystals are transparent and frequently show a more or less deep blue colour.

According to a statement of the Aluminium-Industrie Aktien-Gesellschaft, at Neuhausen, in *Chem. Zeit.*, 1914, p. 1266, the Serpek process had at that time not yet got beyond the experimental stage. The factory in course of construction at Arendal, which was to produce 40,000 tons ammonium sulphate by that process (*ibid.*, p. 343), was to be altered for the Bayer process.

The economy of Serpek's process is proved by the fact that up to the time of reporting, 1 kg. of combined nitrogen, inclusive of all motoric power expended, does not require more than 15 h.p. hours, and Serpek believes that this will be further diminished.

It is there asserted that the conclusion is justified that among all the syntheses of ammonia from atmospheric nitrogen founded upon the intermediary formation of nitrides, the

Serpek process is far away the most perfect and important, and its technical importance is enhanced by its leading also to the production of pure alumina on a very large scale and in a very simple manner. Through Serpek's invention the question of economically fixing the atmospheric nitrogen in the shape of ammonia seems to be solved. The economic exploitation has been taken over by the Société Générale des Nitrures.

Further patents on this process have been taken by Serpek and by the Soc. Gén. des Nitrures (partly in its own name) as follows :—

B. Ps. 7507, of 1909; 13086, of 1910; 25141, of 1911; 8347, 8348, 8349, 10036, 22435, 25630, of 1912; 10975, 11091, 21366, 23740, 24731, 27030, 27971, of 1913; 4287, 22586, 24533, of 1914; U.S. Ps. 987408, 1040459, 1078314, 1078813, 1094171, 1145747, 1145748; Ger. Ps. 238340, 241339, 246931, 246932, 272674; Fr. Ps. 426868, 427109, 435308, 437168, 438209, 450140, 450178, 457650, 457723, 465807.

Ferro-aluminium nitride (45 per cent. Al) is used by the Soc. Gén. des Nitrures (B. P. 27030, of 1913; Fr. P. 470099) for fixing nitrogen. The mass is heated to about 1200°, and by the exothermic reaction the temperature gets up to about 1850°, high enough to convert all the aluminium into nitride. In the place of ferro-aluminium, alloys of iron with silicon, etc., may be used. According to their B. P. 27971, of 1913, nitrogen is fixed on ferro-aluminium by starting the reaction at one or more points in the mass of ferro-aluminium, and then allowing it to propagate of its own accord through the mass. Or the ferro-aluminium is placed in the state of powder, cold or hot, into an atmosphere of nitrogen which may be heated. Or the nitrogen is led to the bottom of a crucible containing ferro-aluminium raised to the necessary temperature. Or the ferro-aluminium is employed in the form of powder in packets wrapped in paper, or in the form of agglomerates. A few per cent. of compounds, capable of accelerating the reaction such as oxides, and, in particular, Al_2, Al_4C_3, or $AlFl_3$, may be added to the Fe-Al. The products obtained may be used for the production of ammonia alone, or both NH_3 and Al_2O_3. In the former case, the product may be treated with limited alkali or alkali metal aluminate, as described in B. P. 10036, of 1912, or the attack may be effected by hot water alone, preferably under pressure. The residue can be used for preparing a fresh supply of ferro-aluminium, to be again treated with nitrogen. If pure alumina is also desired, the product may be treated according to the process of B. P. 13088, of 1910, and the residue, after the removal of Al_2O_3, may be used in the preparation of a fresh supply of ferro-aluminium by adding a further quantity of bauxite and carbon.

Their B. P. 28071, of 1913, prescribes the addition to ferro-aluminium of alumina, or aluminous substances such as bauxite, kaolin, etc., and carbon, or ferro-compounds in which silicium or boron are alloyed with the iron and carbon. Their B. P. 4287, of 1914, prescribes the addition of 10 per cent. calcium carbide to the ferro-aluminium.

Samuel A. Tucker (*J. Soc. Chem. Ind.*, 1913, p. 1143; *Trans. Amer. Electrochem. Soc.*, 1912, x., p. 745) has investigated the Serpek process in his laboratory, in conjunction with Henry L. Read, and obtained very satisfactory results. A further paper of his on that subject is in *J. Ind. Eng. Chem.*, 1913, pp. 139, 191. Other investigations of it were made by J. W. Richards (*Met. and Chem. Eng.*, 1913, xi, p. 137); by Matignon and by Herre (*Chem. Zeit.*, 1914, pp. 317, 341, 894, 909).

Sofianopulos (*Bull. Soc. Chim.*, v., p. 614) has made a similar investigation; also Kohn-Abrest (*Bull. Assoc. Chim. Sucr.*, 1911, p. 1010).

Other processes.—The Badische Anilin- und Sodafabrik have taken out the following patents for producing ammonia by means of aluminium nitride:—

B. P. 5382, of 1910.
Ger. Ps. 236892, 237436, 243839.
U.S. P. 1102715 (Bosch and Mittasch).
Fr. Ps. 418059, 418287.

That process is also described in the patents of Coutagne: Fr. Ps. 436710, 436789, 472465; B. P. 12057, of 1914.

Zänker (Fr. P. 459093) obtains ammonia and alumina from aluminium nitride, by boiling it under pressure with a concentrated solution of alkaline carbonates and with an alkaline-earth oxide.

Zänker (Ger. P. 280686; Fr. P. 458519) also describes a tunnel-furnace for the production of metallic nitrides or cyanides from oxides, carbon or carbonaceous gases, and nitrogen.

Fichter and Oesterheld (*Z. Elektrochem.*, 1915, p. 50) found that the crystals of aluminium nitride, formed in the manufacture of that substance, are produced by sublimation. They found as the best process for preparing pure aluminium nitride: producing a light-arc with aluminium electrodes in a nitrogen atmosphere, and liberating the aluminium nitride formed from the unchanged metal by heating in dilute hydrogen.

Milde (U.S. P. 1115003, assigned to the Aluminium-Industrie Akt. Ges., Neuhausen) converts aluminium nitride by boiling with the hydroxide of an alkaline-earth metal into ammonia and an alkaline-earth aluminate. The latter is boiled with a concentrated solution of alkali carbonate, and the resulting alkali aluminate treated for the production of pure alumina. Or the nitride and alkaline-earth hydroxide are boiled simultaneously with the solution of alkali carbonate, and alumina is prepared from the concentrated solution of alkali aluminate thus obtained.

C. Ellis (B. P. 25630, of 1912) obtains aluminium nitride by blowing reducing gases into a furnace charged with alumina, and allowing them to be burned there.

Giulini Bros. (B. P. 22837, of 1913; Ger. P. 284531; Fr. P. 463232) conduct the manufacture of aluminium nitride and cyanide by the reaction of nitrogen on a mixture of carbon and alumina (etc.), together with an assisting substance, such as an oxide, hydroxide, or salt of a basic metal, in vessels, tubes, etc., formed of or lined with carbon, at a temperature at which the charge does not melt. Such a lining of carbon may be obtained by heating coal to incandescence in a vessel of refractory material with exclusion of air; or a separate inner carbon tube may be employed, fitting inside the outer tube. A large proportion of assisting substance may be used.

Bunet (U.S. P. 1145747) also employs aluminium nitride.

Wolf (*Z. anorg. Chem.*, 1914, lxxxvii., p. 120) prepares aluminium nitride by rapidly heating to 1900° to 2000° in an electric resistance-oven for an hour; nearly chemically pure nitride, containing up to 33·7 per cent. N, is obtained. The volatilization commences at 1850°, with dissociation. The nitride is crystalline, and fuses at 2150° to 2200°.

Badin (U.S. P. 1143842) makes aluminium nitride by passing a mixture of 30 parts bauxite and 12 parts carbon through a coal-dust flame, fed with just enough air to produce CO, to the exclusion of CO

Peniàkoff (U.S. P. 1159989; Fr. P. 465679) makes ammonia by means of double nitrides of aluminium and alkali or alkaline-earth metals.

By Ferric Nitride.

Margoles (Fr. P. 465265) obtains ferric nitride for use as fertilizer, or for the production of ammonia, by submitting ferric oxide at temperatures from 500° to 1200° to the action of atmospheric nitrogen, in the presence of hydrogen or a gaseous mixture containing it. The nitride obtained is treated with steam, to regenerate the ferric oxide and produce ammonia. By adding carbon, cyanides, cyanamides, or (when using sulphide), thiocyanate may be obtained.

Charpy and Bonnerot (*Comptes rend.*, 1914, clviii., p. 994) obtain ferric nitride by heating iron filings in an atmosphere of ammonia to 650° to 700°. The nitride when treated with hydrogen, preferably at 600°, yields ammonia.

T. B. Allen (U.S. P. 1093819, assigned to The Carborundum Co.) prepares ferric nitride by heating silicon carbide and iron in the presence of substantially pure nitrogen.

Frank and Fincke (U.S. P. 1101424) prepare nitrogen compounds by passing nitrogen at 700° to 1000 over an intimate mixture of iron and silicon (or boron) with lime, magnesia, or baryta. Owing to the presence of various bases the mixture does not fuse, and is very active in consequence of the large surface.

Peacock (U.S. P. 1092167) uses ferric nitride in a circular process.

The Soc. Gén. des Nitrures (B. P. 12841, of 1914) uses ferro-aluminium.

By Various Nitrides.

Lipski (*Z. Elektrochem.*, 1909, p. 189) has made extensive investigations on the synthesis of ammonia from the elements by the mediation of nitrides.

Mehner (B. P. 12471, 1895; B. P. 2654, 1897; B. P. 28667, 1903; Ger. P. 88900) prepares nitrides by the electric furnace, in order to transform them into oxides and ammonia.

The nitrides of *chromium*, *molybdene*, and *tungsten*, which at a dark red heat split up ammonia into its elements, ought to have also the reverse action, if there is a catalytic action in question; but Baur (*Berl. Ber.*, 1901, p. 2385) could not obtain any results with them.

Zinc nitride is prepared by K. Kaiser (Ger. P. appl. K53861) by allowing a dry mixture of hydrogen and nitrogen to act upon zinc oxide, mixed with catalytically acting substances, as palladium-iron, uranium, thorium oxide, etc., at temperatures from 400° to 700°; ammonia is obtained from the zinc nitride by the action of steam at 300°.

Barium nitride is used for the manufacture of ammonia by Dafert and Miklauz (B. P. 16597, of 1914).

Coutagne (Fr. Ps. 436710, 457992, and 469554; B. P. 12057, of 1914) describes electric furnaces for manufacturing nitrides by the action of nitrogen at a high temperature on a mixture of oxides and carbon.

Peacock (U.S. P. 1154800 and 1154801; Can. P. 163922) prepares double nitrides and aluminium-carbonitride from atmospheric air. Bucher (Can. P. 163610) describes a furnace for this purpose.

Ammonia from Atmospheric Nitrogen by the Intervention of Cyanides.

The fact that nitrogen combines with carbon and alkalis at a high temperature has been known for a long time; also that in this case cyanides are formed, and that these react with water to form ammonia, *e.g.*, according to the following equations:

$$KCN + 2H_2O = NH_3 + HCOOK$$
$$KCNO + 2H_2O = NH_3 + HKCO_3$$
$$Ca(CN)_2 + 4H_2O = 2NH_3 + Ca(OH)_2 + 2CO.$$

According to Breneman,[1] Dawes in 1835 drew attention to th presence of potassium cyanide in blast-furnaces. After the hot blast had been introduced, the formation of saline masses was observed, containing upwards of 40 per cent. potassium cyanide, with some carbonate. In 1839 Lewis Thompson[2] obtained potassium cyanide by heating coke, potashes, and iron filings in the presence of air to a bright red heat. Fownes and Young[3] repeated his experiments. Most celebrated are the researches of Bunsen and Playfair,[4] who removed every doubt concerning the formation of cyanides in blast-furnaces, and at the same time proposed a method for utilizing this reaction for the actual manufacture of potassium cyanide. In fact a small factory was erected near Paris by Possoz and Boissière to work this process, which was subsequently transferred to Newcastle-on-Tyne; but this had to be given up after great losses. Later on Bramwell made some improvements in the process, but his factory, also near Newcastle-on-Tyne, was likewise stopped after losing a large amount of money. This lack of success was due to the extreme temperature required, causing a large consumption of fuel, much loss of potash by volatilization, and extensive repairs to the apparatus.

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[1] *J. Amer. Chem. Soc.*, xi., Nos. 1 and 2; *Z. angew. Chem.*, 1890, p. 173.

[2] *Dingl. polyt. J.*, lxxiii., p. 281.

[3] *J. prakt. Chem.*, xxvi., p. 407.

[4] *Rep. Brit. Assoc.*, 1845.

Newton (B. P. 9985, 1843) proposed using the gases from vitriol-chambers for the above process, after purifying them by ferrous sulphate.

The first who utilized this process for the manufacture of ammonia was Swindells (B. P., 12th June 1844), by mixing steam with the nitrogen acting on red-hot coke. Further patents were taken by Binks, Armengaud, and Ertel (*Dingl. polyt. J.*, cxx., pp. 77 and 111).

By Barium Cyanide.—In 1860 Margueritte and Sourdeval found (*Comptes rend.*, l., p. 1100; B. P. 1027, of 1860) that caustic baryta is much more active towards nitrogen than potash, because it is neither fusible nor volatile: the former quality prevents the external fusion of the mass, whereby the action of the gases on the interior is impeded; the latter prevents loss by volatilization—both very awkward drawbacks in the case of potash. Still, the manufacture of commercial cyanides or ferrocyanides by the baryta process would seem to be too difficult; but Margueritte and Sourdeval at once aimed at forming the cyanide only as an intermediate product, and utilizing it for the formation of ammonia by the action of steam, thus:—

$$Ba(NC)_2 + 4H_2O = 2NH_3 + Ba(OH)_2 + 2CO.$$

They made a mixture of native barium carbonate with coal-tar, pitch, and sawdust, with or without iron filings, which was strongly ignited in a fireclay retort till the barium carbonate had been converted into a porous mass of barium oxide. Through this they passed at the proper temperature a slow current of air, the oxygen of which had been previously converted into carbon monoxide by red-hot coal: thus barium cyanide was formed. This was cooled down to 300°, and steam was passed through. All the nitrogen of the cyanide is thus evolved as ammonia, and the barium hydrate remaining behind can be used over again. This process did not pay, owing to technical difficulties, and seems to have been given up.

Moerman-Laubuhr, in 1875, took out a Fr. P. 108037 (*Bull. Soc. Chim.*, xxvi., p. 46) for the following process:—Bricks are made of pulverized charcoal or coke and alkaline carbonates, and are exposed in a small blast-furnace to the action of air, previously deprived of oxygen by red-hot coal; the cyanide collects in the melted state at the bottom, and is tapped off from time to time; whereupon it is converted into ammonia by various methods, unnecessary to describe here, as the process evidently turned out a complete failure.

Margueritte and Sourdeval's process was taken up again by L. Mond (B. P. 433, 1882; Ger. P. 21175), who carried it out in the following form:—The barium carbonate is powdered and incorporated with small coke from pitch or oil residues, charcoal, pitch, tar, paraffin residues, and so forth. In lieu of barium carbonate it is possible to employ a solution of barium oxide or salts, or of alkaline oxides or salts; for instance, the solution obtained by lixiviating the used briquettes. The most advantageous proportions are:—Thirty-two parts barium carbonate, 8 parts charcoal or coke, and 11 parts pitch. The addition of alkalis is not of much use. This mixture is formed into briquettes, which it is necessary to heat in a reducing flame till the pitch is coked, and the barium carbonate converted partially or completely into oxide. The briquettes may be broken up into small lumps, and such lumps may also be formed by heating the mixture of barium carbonate or carbon on the hearth of a reverberatory furnace, or in a revolving furnace, by means of a reducing flame until the mass is fritted, when it is discharged and broken up into lumps.

These lumps or briquettes are charged into kilns arranged in the same way as an annular kiln, so that some of the chambers are being heated while others are cooling down or are being filled or emptied. A gaseous mixture, as rich as possible in nitrogen, and containing but little carbonic acid, oxygen, and aqueous vapour, heated to a temperature of about 1400° C., is passed into the chambers filled with briquettes, until a sufficient quantity of cyanogen compounds has been formed. When this is the case, the stream of heated gas is shut off, and cold gas of the same or similar composition conducted into the mass until the temperature has fallen to 500 C. If the aim be to produce ammonia, the stream of gas is now suspended and the material treated with steam; ammonia is hereby formed, is aspirated off, and absorbed or condensed. If, however, the aim be to produce cyanogen compounds, the mixture in the chamber must be cooled to at least 500° C. At this temperature it may then be safely removed, lixiviated with water, and the cyanogen compounds obtained from the solution in the usual manner. In order to obtain ammonia, the mass is treated with steam or a fine spray of water at a temperature of 300° to 500°. The lumps thus dealt with may repeatedly undergo the same treatment, until most of the carbon is consumed. As sources of nitrogen, the gases evolved from the carbonic-acid absorption-apparatus of the ammonia-soda process, and the gaseous mixture obtained by the combustion of coal or coke with the smallest possible quantity of hot air, are the most profitable; and the requisite temperature is most readily obtained by means of a Siemens recuperator, applying this also to the previous heating of the air employed for the combustion. The gases leaving the last chamber which is being heated at the time must be further cooled down by passing them under a boiler or pan, or through a washing-apparatus, before they get into the chamber where the material is just cooling. After having fulfilled this object, these gases, which contain much carbon monoxide, may be burned and used as a source of heat; for instance, for heating air, generating steam, and for other purposes.

For working upon a moderate scale, the following process and plant are recommended:—In a heating-chamber, B (Figs. 231 and 232), four earthenware retorts (A) are arranged in couples. Into this combustion-chamber, heating-gas and air, previously heated in a recuperator, enter by the slits *c*, the products of combustion being forced by the wall *a* to surround the retorts and thoroughly circulate before passing to the recuperator R. The lower parts (H) of the retorts (A) are made of iron, and are either surrounded by water or are kept constantly sprayed by means of the jets *c*. The tubes D serve to introduce the gases rich in nitrogen into the cooling-chambers

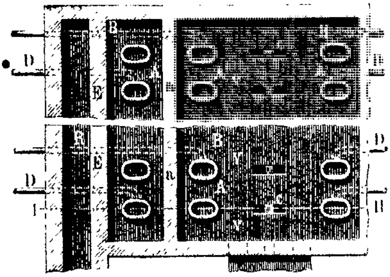


FIG. 231.

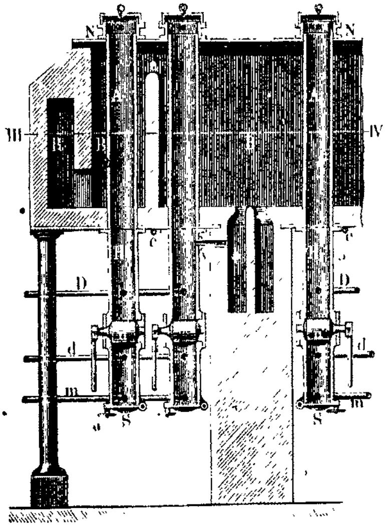


FIG. 232.

H, and by the tubes *d* the passage of steam is effected. The retorts A having been charged with the briquettes, the temperature is raised to 1100° to 1400° C., and nitrogen passed in through D, traversing the mass in H and abstracting heat therefrom. From time to time the tap *u* is closed and portions of the product are removed by the door S, new briquettes being fed in at N. In order to convert the resulting cyanogen compounds into ammonia, the masses taken out of H at a temperature of 300° may be treated in a separate apparatus; or, more simply, the tap *u* is closed, and through the subjacent mass, still at a temperature of 500°, steam is passed by means of the tube *d*, the ammonia formed issuing at *m*. When the formation of ammonia has ceased, the portion of the retort below the tap *u* is emptied; the tap is opened in order to fill that space again, and a fresh charge of briquettes is introduced at the top of A. In some cases it will be found advantageous to use hot producer-gas instead of a cold gaseous mixture containing nitrogen. Since this requires less heat from B, the work done by the retorts will be thereby increased, but the cooling-space H will require to be enlarged, since it is only cooled from without. But the cooling within the space H may also be hastened by passing in cold gases at D, and at the same time hot generator-gases at *v*. In the latter case an opening must be provided in the upper part of H just below *v*, by which the greater part of the cooling gases may escape; and it is best to provide a tap or slide between these two parts. The gases which leave the retorts A contain much carbon monoxide, and may be utilized for heating purposes.

Mond's process, although tried on a somewhat large scale, did not come into practical operation. The process requires a very large amount of heat (as much as 97,000 metrical heat units to 1 kg. mol. cyanide) to be communicated through the earthenware sides of a retort, which wastes too much fuel, even if retorts similar to those of zinc works are employed. This cannot pay whilst so many other sources of ammonia are available; and Mond himself later on turned to preparing ammonia in a much cheaper way from the enormous stock of nitrogen contained in coal, as we shall see later on.

Gros, Goissedet, Bouchardy, and Fossier (Fr. P. 460684) heat balls made of 8 parts barium carbonate, 3 carbon, and 2 tar, to 600° in gas-retorts, recovering the tar by distillation; then place them into an electric furnace heated to 1600°, where they are subjected to the action of a gas containing nitrogen, *e.g.*, producer-gas or air, whereby barium cyanide is obtained which is decomposed by steam into ammonia, carbon monoxide, and baryta.

Another development of the same method has been attempted by L. Q. Brin and A. Brin (B. P. 3089, of 1883), combining with it the manufacture of barium peroxide, according to their B. P. 1416, of 1880 (Ger. P. 15298). They employ two sets of retorts. One of them contains barium oxide, which is kept at a temperature of 600°, and retains the oxygen of the air passed in, with formation of barium peroxide. The remaining pure nitrogen is pumped over into the second set of retorts, which are charged with "barytic coke," at a temperature of 800°. The barytic coke is made from equal parts of barium oxide or carbonate and charcoal powder, agglomerated by coal-tar. Thus the barium is completely transformed into cyanide, which is converted into NH_3, CO_2, and BaO by passing in steam at a temperature of 300°. The second set of retorts is heated by means of producer-gas, and the surplus heat of the fire-gases serves for heating the first set of retorts.

Thorsell (B. P. 11485, 1915) describes some improvements in the production of ammonia from barium cyanide.

Various Cyanides.

Blairs (*Dingl. polyt. J.*, ccxxx., p. 93) employs a cupola filled with a mixture of carbon and potash, heated from the outside. The cyanides volatilize and are condensed outside.

J. Young (B. P. 16046, of 1885) recommends as a suitable material for retorts, destined for manufacturing cyanogen compounds by the above-described processes, non-acid and non-metallic substances. Compressed coke or plumbago answers moderately well; but magnesian limestone answers best. The raw limestone is calcined, ground, mixed with tar, moulded and reburned, exactly as is done for bricks used in the Thomas-Gilchrist dephosphorizing process. [It is more than doubtful whether such retorts would stand the wear and tear of the process, and a "basic" material does not seem to be called for in this case, as the baryta mixture does not fuse.]

Another modification of the above principle is that patented by T. B. Fogarty (B. P. 5361, of 1883). He leads ordinary producer-gas, freed from moisture and in a high state of incandescence, downwards through a tower in which a shower of intimately mixed and finely comminuted carbon and alkali is constantly falling down. At the bottom of the tower is a pit containing water to catch the falling material, provided with an opening for the escape of the gas. A great deal of the nitrogen of the producer-gas is taken up by the carbon and alkali to form alkaline cyanides, which are met in their downward course by a steam-jet introduced into the lower part of the tower. Thus the cyanogen compounds are decomposed, ammonia being formed, which is then washed out by scrubbers. The gas left after this treatment is next conducted into a retort, where ordinary bituminous coal mixed with alkali is undergoing distillation. Here a further combination of nitrogen with carbon and alkali takes place, with formation of cyanogen compounds. Some of these are decomposed by the aqueous vapour in the retorts, but the bulk remains in the coal left behind in the retorts. The producer-gas here serves as a diluent or absorbent of the rich hydrocarbon vapours which are given off by the coal in the early stage of the distillation, and which would otherwise be converted into tar. After leaving the retorts, the gases are again scrubbed for ammonia. When the distillation is finished, the coke is transferred, with as little exposure to the air as possible, into a closed vessel, where a stream of water is allowed to play upon it from the top. The steam thus generated decomposes the cyanides with evolution of ammonia, which passes upwards through the new cool layers of coke above, and with the gases generated simultaneously is led away and recovered by scrubbing.

Later on (B. P. 13746, of 1887; U.S. Ps. 417778 and 615266), Fogarty modified his process. He passes a mixture of air and steam through red-hot carbon, and thereupon through a white-hot retort, filled with powdered carbon and alkali. A feeding-worm constantly introduces alkalized carbon at the top, which lower down meets with nitrogen and steam. The cyanides formed are at once decomposed into NH_3, CO_2, CO, and K_2CO_3. A hydraulic main keeps back the fixed particles mechanically carried along, after which the gases pass through condensers and scrubbers.

De Lambilly (B. P. 16049, of 1890; Ger. P. 63722) mixes equal volumes of air (freed from oxygen by red-hot copper) and coal-gas (freed from all hydrogen and most hydrocarbons by the cupric oxide formed as above). The gaseous mixture is freed by caustic lime from carbon dioxide and steam, and is slowly passed over a mixture of sodium, potassium, or barium carbonate with coke and lime (previously heated till no more CO is evolved) at a white heat and at a plus-pressure of 10 or 15 cm. mercury. The gases have thus time to form cyanides, and only H and CO escape, which are utilized for heating the furnaces. The process can be improved by mixing the mass with oxides, granular iron, nickel, or cobalt. The cyanides formed are mixed with the theoretically necessary quantity of water, and after twenty-four or forty-eight hours the ammonia obtained by the reaction:

$$CNK + 2H_2O = HCOOK + NH_3$$

is expelled by heating in retorts

Quite similar are the processes of J. Young (B. P. 24856, 1893), Mackay and Hutcheson (B. Ps. 6925 and 13315, 1894), J. C. Fell (B. P. 20722, 1889), and others.

Readman (B. P. 6621, 1894) heats a mixture of 1 part carbon and 5 parts barium carbonate with air in an electric furnace. T. L. Willson (B. P. 21997, 1895) passes nitrogen into calcium carbide, to produce the reaction: $CaC_2 + N_2 = Ca(CN)_2$, whereupon ammonia is formed by the action of superheated steam. Mehner (Ger. P. 92810) employs an electric furnace, into which carbon and alkali are introduced from the top, together with air. The gases and cyanide vapours are taken away quite hot and carried into a cooler, filled with coal or coke, where they condense and are treated with steam.

Breneman (*J. Amer. Chem. Soc.*, xi., Nos. 1 and 2) states the following conditions as most suitable for the formation of cyanogen from C and N:—A bright red-heat; absence of oxygen, but little water (more for ammonia); most intimate mixture of all reagents; the presence of a strong base (even ammonia may serve in some cases), preferably potash, or else baryta. Probably ammonia and cyanogen are formed at different temperatures and degrees of moisture. CO and other reducing gases seem to answer the purpose; O, CO_2, and excess of steam are certainly injurious. SO_2 and H_2S are hardly suitable. Hydrocarbons are favourable, and sometimes allow of dispensing with the presence of a base. The influence of pressure is as yet unknown.

The Badische Anilin- und Sodafabrik (B. P. 22038, 1906; U.S. P. 914468; Fr. P. 372714) obtains ammonia from the cyanides of the alkaline-earth metals by heating with water in an autoclave to about 150°. Whilst in the formerly usual process of treating with steam at 300 to 500° there was also a formation of carbon monoxide and free nitrogen, the yield of ammonia by the just-mentioned process is nearly quantitative, and barium formate is obtained as by-product. The cyanides required, especially that of barium, can be prepared in furnaces described in their Ger. P. 190955. Barium cyanide, according to their Ger. P. 197394, can be also obtained from barium cyanamide by treating the latter at temperatures below 1200° with gases containing carbon compounds (producer-gas, etc.).

Their Ger. P. 235662 (Fr. P. 387001) describes the production of alkali or alkaline-earth cyanides or cyanamides by heating compounds of nitrogen and silicon or aluminium (*e.g.* the nitrides) with alkali or alkaline-earth oxides or salts, with or without a flux. To avoid loss of nitrogen, the temperature should not be raised higher than is necessary to produce a homogeneous melt.

Burkheiser (Ger. P. 256893) converts the cyanides in coal-gases first into sulphocyanides and then converts these into ammonia.

Haakh (Ger. P. 281044) prepares ammonia, together with formates, by heating 135 parts potassium ferrocyanide with 260 parts water in a high-pressure vessel to about 200°. Or else spent gas-purifying mass, mixed with excess of lime, is treated with steam of 200° to 250°, until no more ammonia escapes, and calcium formate is obtained by lixiviating the residue.

Bucher's processes for the preparation of sodium cyanide and ammonia have been mentioned *supra*, p. 1089.

Peacock (U.S. P. 1035727, assigned to the du Pont de Nemours Powder Co.) produces a compound of the formula $Al_2C_3N_6$, by mixing finely divided alumina with carbon, in excess of that required to produce the nitride, and subjecting the mixture to the temperature necessary to produce the cyanide, under a pressure of less than 500 mm. of mercury. U.S. Ps. 1031581 and 1031582 refer to the same process.

The Chem. Fabr. von Heyden A. G. (B. P. 5051, of 1913; Fr. P. 457735) make alkali cyanides by treating cyanamide or its polymerides with alkali metals or their alloys and carbonaceous materials.

Lance and Elworthy (B. P. 4409, 1906; Fr. P. 355504) describe the manufacture of ammonium cyanide, and afterwards of other nitrogenous compounds, by passing a mixture of methane, nitrogen, and hydrogen over heated pumice or metallic nickel.

Borchers and Beck (Ger. P. 196323) describe an electrolytic process for the preparation of nitrides from metallic oxides or salts by means of atmospheric nitrogen.

Ashcroft (B. P. 16765, of 1910; U.S. P. 104566) produces alkali cyanamides by heating alkali amides with a stable form of cyanamide or any of its polymerides (dicyandiamide or tricyantriamide), the temperature being increased gradually to 600°. The reaction is:

$$4NaNH_2 + (CN_2H_2)_2 = 2Na_2CN_2 + 4NH_3.$$

The ammonia is collected and used for producing a further quantity of alkali amide (Fr. P. 421851). By adding carbon to the mixture and heating to 750° to 850°, or by heating the alkali cyanamide with carbon, alkali cyanides are produced. His B. P. 10420, of 1914, gives further details on this process.

Further patents concerning the production of ammonia from cyanides have been taken by:

Devaucelles (Fr. P. 429140).

Sulzer-Rieter (Ger. P. 243797; Fr. P. 438905).

F. Hauff (Ger. P. 232878; he works with hydrogen cyanide).

Heys (for Nitrogen Co., Ossining, B. P. 24413, 1910).

Burgeoin (Fr. P. 440331).

South Metropolitan Gas Co. and Evans (B. P. 29047, of 1913; Evans, U.S. P. 1148368).

Lamb (U.S. P. 1123763).

P. E. Williams (B. P. 2841, of 1914).

German patents of Gilmour (No. 73816), Alder (Nos. 12351, 18915, 27334), Nithack (No. 95532), Caro and Frank (Nos. 88363, 92587); U.S. P. of Dankworth (No. 569325).

Calcium Carbide and Cyanamide (Lime-Nitrogen)

Historical Notes (*Chem. Ind.*, 1915, p. 306).—This substance which has now acquired such importance in the industry of ammonia was discovered accidentally in the pursuance of attempts, made by the Cyanid-Gesellschaft, founded by Messrs Siemens & Halske, at manufacturing potassium cyanide from barium carbide, according to a process taken over from the Deutsch Gold- und Silber-Scheideanstalt at Frankfort. This process was not technically successful, but in working at it F. Rothe discovered that alongside of the cyanides also ammonia-like cyanamides were formed; and H. Freudenberg found that also calcium carbide takes up nitrogen, forming not those poisonous cyanides, but cyanamide. At his suggestion Wagner, of Darmstadt, and Gerlach, of Bromberg, made the first experiments at employing the "lime-nitrogen" as a fertilizer. But as the agriculturists are accustomed to employ for that purpose ammonium sulphate, Erlwein, of the firm Siemens & Halske, proposed to transform the amide-nitrogen in a cheap way into ammonia. The question was now to work out the manufacture of lime-nitrogen as a technical process to be carried out on a large scale. The principal merit in that direction (apart from the great merits of A. Frank and N. Caro, see pp. 1127 *et seq.*) is due to Dr Voigt, of the firm Siemens & Halske, who constructed during the years 1902 to 1904 furnaces for that purpose at Martinikenfelde, near Berlin. The first large factory was built in 1905 at Piano d'Orta in Italy, where nitrogen was prepared by fractionating liquefied air. The electric inside heating, now usually employed, was also introduced by Voigt in 1906 at an experimental factory at Siemenstadt, near Berlin. These electric nitrogen furnaces were afterwards installed at Notre Dame de Briançon (France), Martigny (Switzerland), Odda (Norway), Niagara Falls, Osaka (Japan), and Trostberg (Bavaria); and new factories are to be built at Bitterfeld and at Königshütte (Germany), to work with 60,000 and 30,000 kilowatt respectively.

The American Cyanamide Company commenced the manufacture of lime-nitrogen at Niagara Falls in 1910, with an annual production of 12,000 tons. This was increased to 32,000 tons in 1911, and to 64,000 tons in 1912. Since the end of 1914 that firm also supplies *argon*, obtained as a by-product, in technical quantities; it is employed for half-Watt-Wolfram lamps.

The history of lime-nitrogen is discussed by Frank and Caro in *Chem. Ind.*, 1915, p. 445, and Arndt, *ibid.*, p. 446.

According to A. Frank (*Z. f. komp. u. verfl. Gase*, xvi., p. 67), in the year 1914 32 million cbm. of pure nitrogen was produced for the manufacture of lime-nitrogen by fractionating liquefied air, but there is at present no market for the 9 million cbm. of pure oxygen produced at the same time.

We shall in the first instance mention the laboratory investigations made upon this subject, and then describe the technical processes proposed and partially carried out on a large scale for this object. We include in this enumeration also the work referring to the use of other bases, as barium or lithium oxide, for the same purpose.

Scientific laboratory investigations on the fixation of nitrogen by the carbides of alkaline-earth metals have been made by Moissan (*Comptes rend.*, 1894, pp. 503 and 685); Bredig (*Z. Elektrochem.*, 1907, lxix., p. 605); Forster and Jacoby (*ibid.*, p. 101); Rudolfi (*Z. anorg. Chem.*, 1907, p. 170); Kuhling and Berkold (*Ber.*, 1908, p. 28; *Z. angew. Chem.*, 1909, p. 193); Lipski (*Z. Elektrochem.*, 1909, p. 189); Pollacci (*ibid.*, 1908, p. 565).

We here give a short abstract of the results.

Calcium or barium carbide in the *pure* state are very little acted upon by nitrogen; up to 1200° C., they fix little or nothing of it. But the impure technical products do so at very much lower temperatures, so that some of the foreign substances present (chlorides, oxides of various metals, etc.) must exercise a sort of contact action, which is distinctly evident from Frank and Caro's technical results (pp 1129 *et seq.*). Barium chloride alone seems to influence neither the temperature at which the reaction begins nor the total amount of nitrogen fixed, but it seems to favour the formation of cyanide at the expense of cyanamide. But the *oxides* have a very strong action, although it is not yet known which of them are most efficient. They cause the absorption of nitrogen to begin already at 500° or 600° C., and the amount fixed at higher temperatures to be much greater than otherwise, the maximum being reached at 920° to 930° C. If barium chloride, say 10 to 30 per cent. of it, is present at the same time as the oxides, etc., the rate of absorption increases further till the temperature of 1120° to 1130° is reached, and the yield is also decidedly increased thereby.

Rolla (*Ann. Chim. anal.*, 1914, ii., p. 301; *J. Soc. Chem. Ind.*, 1915, p. 27) investigated the composition of the gases given off in passing air over a mixture of barium oxide and carbon heated to above 1000°, to produce barium cyanide and cyanamide. To ascertain the character of the combustible gases produced in the second stage of the process, pure barium cyanide was heated in nitrogen to various temperatures between 100° and 500°, then treated with steam, and the products analysed. They contained per gram of NH_3 produced from 165 to 459 c.c. CO, 399 to 1118 c.c. H_2, 211 to 401 c.c. CH_4, and 59 to 94 c.c. CO_2. Gas of the maximum calorific value is obtained between 300° and 400°. Probably barium formate is formed as intermediate product, and is decomposed in various ways according to the conditions.

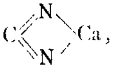
Tucker and Moody (*J. Amer. Chem. Soc.*, xxxiii., p. 1478) investigated the action of lithium carbide as absorber of nitrogen. Tucker and Wang (*Trans. 8th Cong. Appl. Chem.*, xa., p. 121) that of strontium carbide.

Carlson (*Z. angew. Chem.*, 1914, iii., p. 724; extract, *J. Soc. Chem. Ind.*, 1915, p. 351) describes the products obtained by heating crude calcium cyanamide at moderate temperatures, viz., dicyanodiamide, dicyanodiamidine, guanidine.

A study of the fixation of nitrogen by calcium carbide has been made by Pollacci (*Z. Elektrochem.*, 1908, p. 565). He finds that potassium carbonate exerts a catalytic action on the absorption of nitrogen by calcium carbide, lowering the temperature required. The best results are obtained with an addition of 4 per cent., and by working at a pressure of 2 atmospheres, at 900° to 950°, when after one hour 23·0 per cent. of N was found to be converted into calcium carbide.

According to N. Caro (*loc. cit.*, p. 1128), technical calcium carbide, obtained by fusing lime and coal together in the electric-light arc, contains, besides the carbide, lime, sulphides, phosphates, carbon, carbides undecomposable by water, etc., which have a strong influence on the absorption of nitrogen, on the time it is going on, and on the temperature required. Carbides of the same chemical composition, if produced in furnaces of different construction, behave differently in consequence of their different physical properties; and so does even the same carbide, according to whether it is employed straight from the furnace, or after being kept in stock for some time. These differences explain why some chemists have obtained favourable results by making various additions, *e.g.*, chlorides; but in working on a large scale these additions are unnecessary, the reaction being sufficiently regulated by a suitable comminution of the substance.

The essential constituent of lime-nitrogen is *calcium cyanamide*, $CaCN_2$, which in some reactions acts as if its formula were $Ca=N—C\equiv N$, in others as



that is in the first case as the calcium salt of cyanamide in the second case as the calcium salt of the diimide. According to Löhnes, the phenomena occurring by the action of bacteria on lime-nitrogen point at the diimide formula, since both atoms of nitrogen are affected contemporaneously and in the same way. Technical lime-nitrogen contains also other nitrogen compounds: urea, calcium carbaminate, guanidine, etc., not much of them in the fresh state, but more so after being kept for some time, or after the action of steam.

Manufacture of Pure Calcium Carbide.—According to De Kay-Thompson, Gonzalez, and Blake (*Met. and Chem. Eng.*, 1914, p. 779), the preparation of pure calcium carbide from calcium filings and purest carbon could not be effected; no more that from calcium hydride and carbon, nor by the action of acetylene on calcium or calcium hydride. Satisfactory results were only obtained by passing acetylene into a solution of calcium in liquid ammonia, a process already employed by Moissan.

Technical Processes for the Preparation of Calcium Carbide and Cyanamide (Lime-Nitrogen).

Most important work in this field has been done by Professor Frank and Dr Nikodem Caro, who act on the principle that *carbides* of sodium, calcium, baryum, etc., are formed in the first instance, and these are only subsequently transformed into *cyanides* by the influence of nitrogen under special circumstances. Berthelot already in 1869 (*Comptes rend.*, lxvii., p. 141) had assumed this to be the case, and had also shown that under the influence of the electric arc acetylene combines with nitrogen to form potassium cyanide. At that time nothing could come out of this, as there were no technical methods known for producing the carbides. Only since Moissan's classical work in this field had been done, and since Willson after the erection of the first calcium carbide factory at Spray (North Carolina), in 1895, had demonstrated the possibility of producing these compounds in a cheap way, it became possible to transfer Berthelot's work to the sphere of industrial chemistry.

The fundamental work in this direction has been done by Frank and N. Caro in the years 1895-1902. On this Caro has reported at length in a lecture reprinted in *Z. angew. Chem.*, 1906, pp. 1569 *et seq.*; and Frank, in *J. Soc. Chem. Ind.*, 1908, pp. 1093 *et seq.*

The following is a list of the patents of Frank and Caro, mostly taken out in their own names, but partly in that of the Cyanid-Gesellschaft, Berlin (in which the world-renowned firm of Siemens & Halske plays a prominent part), which has taken them over, and in that of patent agents:—

Ger. P.	88363, of 1895,	preparation of cyanides from carbides.	
„	92587, of 1895	(the same—addition to the former).	
„	95660, of 1896	„	
B. P.	15066, of 1895	(the same).	
Fr. P.	249539, of 1895	„	
Ger. P.	108971, of 1898,	preparation of	cyanamide salts.
„	116087, of 1898	„	cyanides.
„	116088, of 1898	„	„
Fr. P.	289828, of 1898	„	nitrogen compounds.
B. P.	25475, of 1898	„	„
Ger. P.	134289, of 1900	„	ammonia from cyanamides.
„	152260, of 1901,	artificial nitrogenous fertilizers.	
„	157503, of 1902	„	
Fr. P.	319897, of 1902	„	
B. P.	15976, of 1902	„	
„	17507, of 1902	„	
Ger. P.	150878, of 1902,	calcium cyanamide (Stomps).	
Fr. P.	328031, of 1902	„	
B. P.	16298, of 1902	„	
Fr. P.	382743, of 1907,	nitrogen compounds from carbides; and two additions.	

B. P. 21786, of 1906 (by Frank and Voigt).
B. P. 5314, of 1907, nitrogen compounds from carbides (Bloxam).
Ger. P. 203308, nitrogen compounds of alkaline earths from carbides.
" 204882, pure nitrogen from combustion gases.
" 212796 and 272638.
U.S. P. 1006927.

The history of the formation of cyanogen compounds from free nitrogen, which goes back to the year 1813, has been described in detail by N. Caro (*Chem. Ind.*, 1895, p. 287, and *Z. angew. Chem.*, 1906, p. 1569); Frank (*J. Soc. Chem. Ind.*, 1908, p. 1093); Caro ("Die Stickstofffrage in Deutschland," 1908), and by the same in a lecture given at the International Congress for Applied Chemistry in London, in 1909 (printed in *Z. angew. Chem.*, 1909, pp. 1178 *et seq.*).

We now give a short outline of Frank and Caro's principal results, going into more details upon their later patents. Calcium (or barium) carbide is treated at red-heat with atmospheric nitrogen, *e.g.*, such as is obtained by passing air through red-hot copper, contained in outwardly heated retorts, which fixes the oxygen and allows the nitrogen to escape. Of course the nitrogen may be obtained by any other means, *e.g.*, the Linde process, consisting in the fractional distillation of liquid air. This nitrogen is passed through a retort, containing the carbide; as the reaction is exothermic, the retort requires only at first heating from the outside; later on, the process of fixing the nitrogen goes on by itself, until all the carbide has been consumed. The reaction consists in the formation of calcium (or barium) cyanamide and cyanide. Possibly the latter is formed in the first instance:

$$CaC_2 + N_2 = CaC_2N_2,$$

and is later on converted into cyanamide:

$$CaC_2N_2 + N = CaCN_2 + CN.$$

When working with calcium carbide, at the proper temperature (which is 700° to 800° for barium carbide, and 1000° to 1100° for calcium carbide), only traces of cyanide are left. The product obtained, consisting essentially of cyanamide, mixed with carbon (graphite), has been called "Kalkstickstoff" (lime-nitrogen); it contains 20 to 24 per cent. nitrogen, and may be used directly as a fertilizer, in competition with nitre or ammonium sulphate. But it may also be employed for the production of ammonia, by being spread on trays and subjected to the action of superheated steam:

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3.$$

In lieu of the carbides, the substances giving rise to their formation may be employed at the same temperatures. In this case mixtures of the oxides and carbonates with carbon are employed, and the reaction is:

$$CaCO_3 + 3C + N_2 = CaN_2C + 3CO.$$

Some very essential points must be kept in view in this process. The reaction is reversible at temperatures above those just named:

$$CaC_2 + N_2 \rightleftarrows CaCN_2 + C.$$

According to Caro (*loc. cit.*) the reversion takes place at 1360°, if carbide obtained in a blast-furnace, containing 82·3 per cent. CaC_2, is employed. Larger quantities of lime lower the temperature of reversion. On that account, the carbide cannot be directly azotized, when it comes out of the electric furnace, but must be allowed to cool down; and as it is not permeable for the nitrogen in that state, it must be reduced to powder. The heat produced by the absorption of nitrogen by the carbide may also raise the temperature to the critical point; this must be prevented by constant agitation, and by employing mixtures with high specific heat. The best plan is putting the comminuted carbide into a heat-insulated vessel, heated from within by an electrically heated carbon rod, and passing in nitrogen. After some time the electric heating may be interrupted; the reaction then goes to the end by itself. The total energy required for preparing the carbide, azotizing, machine-work, grinding the carbide and the lime-nitrogen, moving the air and liquefying it by Linde's process, amounts to less than 3 h.p. years per ton of nitrogen fixed in the shape of lime nitrogen.

The same subject is treated in the Fr. P. 382743, 1907, of the Berliner Cyanid-Gesellschaft, and in the B. P. 21786, 1906, of A. Frank and M. Voigt.

The Badische Anilin- und Sodafabrik in their Ger. P. 235662 describes the preparation of alkali or alkaline-earth cyanides or cyanamides by heating compounds of silicon or aluminium (*e.g.* the nitrides) with alkali, or alkaline-earth oxides or salts, but not higher than is necessary to produce a homogeneous melt. The U.S. P. 1022351 (of Bosch and Mittasch) describes the same process.

Schick and Aktien-Gesellschaft für Stickstoffdunger (Ger. Ps. 260469 and 450435; Fr. P. 430060; U.S. P. 1008927) manufacture calcium cyanamide by adding halogen salts (which need not be absolutely dry), little by little, to molten calcium carbide, as it leaves the furnace in which it is produced; the solidified material, whilst still red hot, is treated with nitrogen.

F. Bayer & Co. (B. P. 2311, of 1912) obtain cyanamide from the crude cyanamide in the form of an insoluble lead compound, which is then decomposed by dilute sulphuric or hydrochloric acid; the cyanamide is isolated by filtration and evaporation *in vacuo*. *E.g.*, 100 kg. of crude calcium cyanamide are added to 450 kg. of 20 per cent. sulphuric acid mixed with 300 kg. ice; the filtered liquid, if alkaline, is rendered slightly acid, again filtered and mixed with 100 litres of 20 per cent. ammonia solution and 180 kg. of lead chloride (in aqueous paste); the lead cyanamide is again filtered off. The U.S. P. (by Engelmann and Merkel) is 1102892.

Weaver (U.S. P. 1093749) describes an apparatus for the production of cyanamides, consisting of a chamber containing inclined grate-bars which can be constantly agitated, and an adjacent heating-plate with embedded gas-heating pipe; the plate is heated by a burner beneath. Calcium carbide is fed continuously over the plate and bars, and nitrogen is forced upwards through the (perforated) bars. The embedded gas-heating-pipe may receive nitrogen from an external source or gas from the heating zone for recirculation.

Lidholm and the Dettifoss Power Co. (B. Ps. 18207, of 1911; 28629 and 28524, of 1913; Canad. Ps. 164510, 164647; Fr. P. 465379) produce calcium cyanamide by introducing calcium carbide continuously into a highly heated furnace, supplied with nitrogen. The block of cyanamide when formed is immediately removed into a vessel with perforated sides, resting on the furnace bottom. The latter is removable and quickly replaceable by another furnace bottom, carrying an empty collector, so that no heat is lost when changing collectors. Other patents of theirs (B. Ps. 3545 and 3546, of 1914; Fr. P. 465473; Ger. P. 274472) describe a rotary furnace for the same purpose, containing injectors for producing a circulation of the nitrogen and working under pressure. Their U.S. Ps. are 1004509 and 1009705. Another process of the same inventors (U.S. P. 1125350; Fr. Ps. 469045 and 469046; B. P. 3545, of 1914) brings nitrogen under pressure into contact with heated calcium carbide, mixed with sand, to prevent fusion at a temperature at which the reaction is instantaneous. The product is suddenly chilled below its dissociation temperature. Lidholm's Ger. P. 277525 prescribes preparing ammonia from lime-nitrogen by the action of alkali hydrates or carbonates. Their B. P. 3547, of 1914, describes the instantaneous production of calcium cyanamide by heating CaC_2 and N separately or simultaneously much above the reaction temperature. The finely powdered carbide is sifted into nitrogen, passed through a tube, highly heated by the electric current through ring contacts, through charcoal between an outer shell and the central tube.

C. White (B. P. 17933, 1913) makes cyanides and cyanamide by heating a mixture of 14 parts calcium carbide and 20 parts sodium chloride to 750° to 900°, and passing nitrogen for twelve to twenty-four hours at a pressure of 10 lb. above atmospheric pressure over it.

Peacock (U.S. P. 1129514, assigned to the International Agricultural Corporation) heats phosphate rock with carbon to 1500°, removes the resulting phosphorus and carbonitride vapours under diminished pressure, and separates them by oxidizing the former and passing into water. The carbonitride is decomposed to ammonia by heating the solution to 200°. His U.S. P. 1129505 extends this process to orthoclas and similar silicates.

Bredig and Fraenkel (Fr. P. 382188) prepare cyanides, cyanamides, and nitrides by heating calcium carbide with nitrogen under pressure, preferably mixed with a catalytic substance, such as certain salts or carbon powder.

A French patent (382743, of 1907) has been obtained by the Cyanid-Gesellschaft for the manufacture of nitrogen compounds by means of carbides. When the carbide of a metal, belonging to the group of alkalis or alkaline earths, is treated in a current of nitrogen at one point, the reaction will propagate itself throughout the mass, if the necessary initial temperature is reached. The preliminary heating may be brought about electrically, or by passing heated nitrogen over the carbide, which itself may be heated moderately, or by the addition of another constituent to the nitrogen or the carbide (*e.g.*, oxygen or aluminium powder), which shall, by reaction with some substance present, liberate the necessary heat.

The Ger. P. 203308 of the Cyanid-Gesellschaft, Berlin, attains the same purpose by adding salts of cyanamide to the carbide, *e.g.* calcium cyanamide. This avoids the addition of alkaline oxides, carbonates, dioxides, fluorides, etc., and produces an article of high percentage, and well adapted for manurial purposes.

To this patent additions have been made, dated 11th and 12th October 1907:—(1) The nitrogen is made to pass over the mass in a direction opposite to that in which the reaction is being propagated. This prevents local fusion. To avoid an aggregation of the particles, indifferent substances, such as carbon, wood, crude calcium cyanamide, etc., may be added. (2) For the purpose of starting the reaction by means of electrical heating, vertical cavities are constructed in the mass, formed of some conducting material which is destroyed as the temperature rises and the cohesion of the mass increases. The electro-heaters are thus introduced without coming into actual contact with the material. The carbide is surrounded by a layer of some porous substance, not affected by nitrogen, *e.g.* sand, which protects the walls of the containing-vessel and ensures a more uniform distribution of the gas.

Bazzano e Zanardo (Fr. P. 456826) mixes the calcium carbide, before treating it with nitrogen, with so much calcium cyanamide that a friable, instead of a compact, product is obtained, and fully utilizes the heat of reaction in heating successive charges.

Fujiyama (B. P. 9259, of 1914; U.S. P. 1126000; Fr. P. 471377) burns pulverized carbides in a closed chamber and introduces nitrogen to combine with the burning substance, more material being added to keep the product covered with a layer of carbide. Decomposition is prevented by cooling the chamber.

Peacock (U.S. Ps. 1129512 and 1129513) describes an electric resistance furnace for the manufacture of nitrogen compounds, consisting of a vertical rectangular shaft with two horizontal electrodes placed opposite one another. The charge is supplied from above, and the solid product removed from below by a conveyor. Nitrogen is introduced by two opposite valved pipes below the electrodes, and the gaseous products are removed by similar pipes above. The supply of material and of nitrogen and the removal of the gaseous products and the solid residue are continuous. The temperature of the reaction zone between the electrodes is regulated by the proportion of carbon in the mixture, the rate of passage through the zone, and the amperage of the current supplied.

The Ger. Ps. 282213 and 285699 of Krauss, Stahelin, and the Akt. Ges. f. Stickstoffdünger claim a process for the uninterrupted production of nitrogen compounds from metallic carbides and nitrogen by carrying the carbide mechanically by means of an endless belt, a set of cars, or the like, through a canal furnace, consisting of a preheating-, reacting-, and cooling-space, through which a regulated current of cold nitrogen gas is conducted in the opposite direction. Or else the metallic carbide is placed on shelves in the compartments of an annular furnace, provided with a heating arrangement capable of regulation, in which a heated current of nitrogen can be passed from one chamber to another, or else cold nitrogen into every chamber. The utilization of nitrogen is so considerable that, when the suitable temperature has been reached, the supply of heat from without can be almost entirely suppressed. At the same time stoppages in the machinery and injurious over-heating of the nitrogen compounds are avoided. The Fr. P. is 464750.

The Bosnische Elektrizitäts Akt. Ges. at Vienna in their Ger. P. 283276 describe special forms of furnaces for preparing calcium carbide.

Krauss (Ger. P. 267595) separates calcium cyanamide from the impure solution by means of carbon dioxide.

F. W. Mahon (Fr. P. 456765) purifies commercial calcium cyanamide from carbide and lime by treating it with cold water, granulating, sifting, and drying. The reactions with water are:

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$
$$CaO + H_2O = Ca(OH)_2.$$

According to *Chem. Zeit.*, 1915, p. 320, the Aktieselskab North-Western Cyanamide Co., at Odda in Norway, has recently succeeded in preparing from the crude cyanamide a granulated product with 16 per cent. nitrogen, which is better adapted to agricultural purposes than the somewhat dusty product formerly made, for it contains the lime in the shape of hydrate and therefore causes no caustic action on germinating plants. The dry grains of the new product are easier to manipulate than the oily powder. The nitrogen seems to be present in it in a more active form than in ordinary lime-nitrogen. A granulating works for daily producing 350 tons of the new product has been just started.

The Nitrogen Company, Ossining, New York (Ger. P. 270662), produces alkaline cyanides and cyanamides in continuous work by the employment of a reacting-metal, electrolytically produced, and substances furnishing carbon and nitrogen.

Ungnade and Nolte (Ger. P. 268882) obtain a fertilizer containing nitrogen and phosphoric acid in a form soluble in water, by treating lime-nitrogen with a mixture of phosphoric and sulphuric acids.

Peacock (U.S. Ps. 1129507 to 1129519, and 1129721) describes the production of the carbonitrides of silicon, boron, aluminium, potassium, calcium, and electric furnaces suitable for that object.

Becket (U.S. P. 1137567) makes calcium carbide by mixing lime with a combining proportion of coking coal containing sufficient bituminous material to form a mechanically strong aggregate, suitable for furnacing, coking the mixture in a by-product oven, and recovering ammonia and other volatilized products, and then embedding electrodes in the charge and smelting to form carbide.

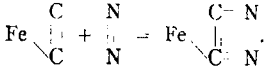
Washburn (*Met. and Chem. Eng.*, May 1915; *Chem. Trade J.*, 1915, pp. 57, 127) describes in detail the cyanamide process as carried out in North America, where the American Cyanamide Co. alone produces cyanamide of the value of $15,000,000, 80 per cent. of which is sold for fertilizing processes.

W. S. Landis (*Met. and Chem. Eng.*, 1915, xiii., pp. 213-220) gives a description of the cyanamide process of the American Cyanamide Co. at Niagara Falls. High-grade materials are necessary for successful operation; the nitrogen employed is obtained from liquid air. The calcium carbide, crushed to pass a 100-mesh sieve, is treated in small ovens (½ to 2½ tons capacity), special precautions being necessary to avoid a reversal of the reaction. The product from the ovens ("lime-nitrogen"), containing about 22 per cent. N and 1 per cent. carbide, is finely ground (great care being required to avoid explosions) and stored in silos. For agricultural purposes it is partly hydrated to decompose the contained carbide, and then "oiled" to render it dustless for storage. This partial hydration requires special attention since, particularly at temperatures above normal, calcium cyanamide tends to become transformed (by the action of water) into a variety of organic compounds of inferior manurial value. Calcium cyanamide is also employed for the manufacture of ammonia, by subjecting a mixture of it with water to the action of heat and high pressure; for case-hardening iron and steel, and for the production of crude sodium cyanide for metallurgical purposes by melting with sodium chloride.—A process is now being developed for converting the ammonia obtained from calcium cyanamide into a fertilizer consisting largely of ammonium phosphate. This product, "ammophos," contains over 13 per cent. NH_3 and 45 to 50 per cent. P_2O_5, and when mixed with high-grade potash salts will make a complete fertilizer about six times as much concentrated as the average grades now available. The world's production of cyanamide (from fourteen factories) during 1914 was about 300,000 tons, the present annual output of the Niagara Falls plant being 64,000 tons.

The American Cyanamide Co prepare their nitrogen by removing the oxygen from air by means of red-hot copper sponge, and reducing the copper again by illuminating-gas. Their factory is described in *Met. and Chem. Eng.*, xii., pp. 265 *et seq.* The gas-works produces about 50,000 cbm. gas in twenty-four hours; the coke obtained thereby serves for the production of calcium carbide.

The North-Western Cyanamide Co. prepares from the dusty crude cyanamide up to 350 tons per day of a granular product, containing 16 per cent. N, and the lime in the form of hydrate, which does not act destructively on the germinating plants.

H. W. Lamb (U.S. P. 1123763) employs non-saturated metallic carbides, such as ferric carbide, barium carbide, etc., for binding atmospheric nitrogen, according to the equation:



He describes a furnace for preparing ferric carbide from ferric oxide and coke, coal, or pitch. The absorption of nitrogen by the carbide is but slow at 1150°, but quickly increases at higher temperatures, and is very strong at 1850°. The nitrogen is prepared by passing air over red-hot coke and removing the CO_2 by lime water.

S. Peacock (U.S. P. 1123584) roasts sulphur or sulphur ores in such a way that all the oxygen of the air is combined with S to SO_2 or SO_3. The roasting-gases, containing about 80 per cent. N and 20 per cent. sulphur oxides, are passed over red-hot coal at about 800°, whereby compounds are formed which, on being decomposed by water or steam, yield NH_3, or when employing dilute sulphuric acid, ammonium sulphate, together with CO and SO_2.

Sinclair (B. P. 15713, 1913; 9821, 1914; Fr. P. 474882) describes a process and apparatus for obtaining granulated calcium carbide.

Uses of Calcium Cyanamide (Lime-Nitrogen).

This product is largely used directly as a *fertilizer.*

The use of calcium cyanamide as a manurial agent is described in *Bull. Imp. Inst.*, 1911, pp. 44 and 122. According to Lumina (*Atti R. Accad. Lincei*, xxiii, pp. 2, 659), it is in that respect superior to ammonium sulphate and nitrate.

The Prussian Minister of State for Agriculture, etc., has issued a prize competition, dated 1st April 1915, for investigations on the action of lime-nitrogen as fertilizer under various conditions, and for removing the trouble caused in its practical application by the deleterious dust created thereby.

Production of Ammonia from Calcium Cyanamide.

Lime-nitrogen is not merely employed as it is for agricultural purposes, but also for preparing many substances important for industry and agriculture, its nitrogen being present in a particularly reactive form. Its most important application is for the production of *ammonia*, which, when employing an excess of water, goes on quantitatively and causes no special expense since, when employing steam for that reaction, the whole of the lime and one-third of the carbon used up for the carbide melt are recovered in a shape in which they can be used again for the manufacture of calcium carbide. If water is employed, in which case hydrated lime is formed, the expense of the transformation is partially covered by the *graphite* recovered from the residue. This is described in the B. P. 5713, of 1911, by Collett and Eckardt

A number of patents have been taken out for the conversion of calcium carbide or lime-nitrogen into ammonia, by the Gesellschaft für Stickstoffdunger (Ger. P. 108706; Austr. P. 36444); by the Oesterreichische Verein fur chemische und metallurgische Produktion (Austr. P. 39777; Ger. Ps 251934 and 276720); by the Compagnie pour la fabrication des Compteurs (Fr. P. 407164); by Collett and Eckardt (U.S. P. 1503433; Norw. P. 19973), who by contemporaneous action of steam and sulphur dioxide on calcium carbide produce ammonium sulphite; by Landis (assigned to American Cyanamide Co.), U.S. Ps. 1163095, 1154640, 1149653.

In order to prepare ammonia from the cyanides of the alkaline-earth metals, the Badische Anilin- und Sodafabrik (U.S. P. 914468, taken by Bosch; Fr. P. 372714), instead of treating it, as formerly usual, with water at temperatures between 300° and 500° C. (which leads to the formation of CO and H), heats the crude cyanides (400 kg., coarsely ground) with water (600 litres) in high-pressure apparatus slowly up to 150° C., until the saponification is complete. The NH_3 is then let off, together with steam, and the perfectly pure gas is treated in the usual manner. The yield is nearly quantitative, and from the residue *formic* acid can be recovered in almost the theoretical quantity. (The English patent for this process is taken out in the name of J. V. Johnson, B. P. 22038, 1906.)

According to the B. Ps. 25260, of 1912, and 9564, of 1913; Fr. P. 458951 of the Badische Anilin- und Sodafabrik, they extract the ammonia from gaseous mixtures obtained by synthetic processes, by passing the gases in the same direction as an absorbing liquid through a system of tubes which may be arranged in series, and supplied respectively with solutions of ammonia of progressively diminishing concentration. Or else the absorption is effected under a pressure exceeding 10 atmospheres, in a series of tubes in such a way that the gases and absorbents move in opposite directions as regards the series of the whole; but in each unit of the series they move in the same direction.

Heinrich Koppers, Essen a. d. Ruhr (Ger. Ps. 268185, 285354), produces ammonia from lime-nitrogen, made with water into a paste, by means of steam in such a way that after absorbing the ammonia in a saturator the gases and steam, after being heated up, can be used over again for expelling the ammonia from lime-nitrogen.

The Oesterr. Verein fur chemische und metallurgische Produktion, at Aussig (Ger. P. 251934), produces ammonia from lime-nitrogen and water by heating up to 180°, obtaining this heat by employing a column of liquid of sufficient height, in a series of vessels combined in such a way that each of them may serve as first, second, third, etc.; the pressure being obtained by the combined height of liquid in all the vessels.

Lohnis (*Z. Garungsphysiologie*, 1914, v., p. 46) ascribes the production of ammonia from cyanamide in the soil to the action of certain fungi.

A French patent of the Aktien-Gesellschaft fur Stickstoff-dünger, 375979; and a B. P. 9407, of 1907, of the same, together with C. Krauss; also a Ger. P. 198706, of 1907, prescribe accelerating the decomposition of cyanides and cyanamides by the addition of calcium chloride. Powdered calcium cyanamide is mixed with an equal weight of a concentrated solution of $CaCl_2$. The paste solidifies on standing; it is then broken into pieces and heated in a retort, the ammonia evolved being collected. Towards the end of the reaction a little steam may be injected, in order to prevent a decomposition of ammonia in contact with the hot sides of the retort.

Zamore and Carlson (U.S. P. 1042746) treat lime-nitrogen with 15 to 50 per cent. by weight of dilute nitric acid containing 3 to 25 per cent. HNO_3, cooling the mass during the treatment.

Further patents on the preparation of ammonia from cyanamides :—

Bayrische Stickstoffwerke (Ger. P. 244452).
Washburn (U.S. P. 1006927).
Ashcroft (B. P. 10420, of 1914).
The Nitrogen Products Co. (Fr. Ps. 455729, 474023).

A further important employment of lime-nitrogen is the manufacture of *cyanides*, for which an experimental factory has been erected at Spandau. In this case a fluxing-agent is added, and the reaction: $CaCN_2 + C = Ca(CN)_2$ goes on quantitatively, although it is endothermic, by means of special apparatus (Erlwein, *Z. angew. Chem.*, 1903, p. 553).

The dicyandiamide obtained from lime-nitrogen has found an application as an addition to *explosives*, in lieu of ammonium oxalate, its action being superior to the latter.

The *graphite* formed during the production of lime-nitrogen can be separated cheaply and in a very pure form by a process worked out by Frank, Caro, and Jacoby, and they state that the cost of converting the nitrogen into lime-nitrogen is entirely covered by the value of this graphite. Caro further reports on the application of lime-nitrogen to the manufacture of potassium cyanide, as well as to the conversion of iron into steel, and to other purposes into which we cannot enter in this place.

Storage of Calcium Cyanamide.—Burgess and Edwards-Ker (*Chem. Trade J.*, 1915, p. 198) report on the influence of air and moisture on it. To prevent loss of nitrogen, paper bags should be used in stripping, and the material worked into the soil quickly.

Statistical Notes on the Industry of Calcium Cyanamide (Lime-Nitrogen).

The *Chem. Zeit.*, 1907, p. 527, contains a glowing report on the development of the industry of calcium cyanamide. Its efficiency for agricultural purposes is stated to be quite on a par with that of nitrates. The problem of utilizing the nitrogen of air may be taken as resolved now, and at an early future this will be the only source of nitrogen compounds for fertilizers.[1] The Società generale della Cianamide at Rome is the owner of the patents in that line, also those of Frank and Caro. Special limited companies have been established in Germany, England, Italy, Austria, France, and Switzerland, for exploiting them. The factories already at work or in course of erection are, in Germany, Trostberg (15,000 tons), Westeregeln (45,000 tons), Bromberg (2500 tons cyanamide per annum); Alby, in Sweden (17,000 tons); Odda, in Norway (12,500 tons); Piano d'Orto, in Italy (10,000 tons); Dalmatia (10,000 tons); Notre Dame de Briançon, in Savoy (3750 tons); Martigny, in Switzerland (3750 tons).

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[1] This is an overstatement of the case! According to Wagner and other authorities, the manurial value of "lime-nitrogen" is only four-fifths of that of "nitric-nitrogen."

According to a report in the *Z. angew. Chem.*, 1909, p. 1040, several of these establishments were at that time working very successfully, and were largely increasing their plant, especially those working with water-power in Italy, France, the United States, and Canada.

According to *Engineering*, 1914, xcviii., pp. 267 *et seq.*, the Odda works (in Norway) have been enlarged to produce 85,000 tons of calcium carbide per year, and a cyanamide plant of 80,000 tons capacity has been built. Other plants in Sweden have been enlarged, and 1,000,000 h.p. of water rights have been secured in Norway and Iceland for the ultimate production of 2,000,000 tons of cyanamide. *Ibid.*, pp. 294, 351, 465 (1914), the works are described in detail. Nitrogen is obtained by the fractional distillation of liquid air. There are 604 furnaces for making cyanamide, each of which, working at about 1150°, converts 450 kg. CaC_2 into cyanamide in thirty hours.

In Germany the Bayrische Stickstoffwerke produce 20,000 tons lime-nitrogen, with 15,000 h.p. (water-power). Another German works produces 10,000 tons lime-nitrogen per annum by means of lignite. According to A. Frank, in *Chem. Zeit.*, 1914, p. 1261, in that year in three German factories 70,000 tons lime-nitrogen was produced. More nitrogen is made available by this method for the same amount of electric energy than by the electrical production of nitric acid.

In *Z. angew. Chem.*, 1915, p. 199, Rassow gives the following statistics concerning lime-nitrogen. The production of it in the whole world has been :—

1906	500 tons	1911 .	52,000 tons	
1907	2,200 „	1912 .	95,000 „	
1908	8,300 „	1913 .	97,000 „	(estimated)
1909	16,000 „	1914 .	220,000 „	„
1910 . . .	30,000 „			

The quantities consumed in Germany:—

1912 to 1913	60,000 tons
1913 to 1914	80,000 ,,

P. F. Frankland (*J. Soc. Chem. Ind.*, 1915, p. 310) states that £5,000,000 capital is already embarked in the calcium carbide industry by various companies of Europe and America. About 120,000 tons is produced annually, about one-quarter of which in Germany.

Washburn, at the Atlantic City Meeting of the American Electro-chemical Society in April 1915 (according to *Chem. Zeit.*, 1915, p. 643) stated that the annual productive power of the plants employed for producing arc and cyanamide products amounts to 90,000 to 100,000 tons combined nitrogen, of a value of $25,000,000 at the works. Two-thirds of this is cyanamide, one-third other nitrogen compounds. The American Cyanamide Company can produce at their works at Niagara Falls (Canada) cyanamide containing half as much nitrogen as all the arc products of the whole world. Most of the cyanamide passes directly into consumption (for fertilizing purposes) without undergoing any manufacturing operation. The just-mentioned American Company sells 80 per cent. of their total production in that shape; besides it manufactures ammonia, urea, cyanides, and recently argon for illuminating purposes.

Analytical Methods for Cyanamides.

Stutzer and Stoll (*Z. angew. Chem.*, 1910, p. 1873) estimate the nitrogen contained in "lime-nitrogen" in the form of cyanamide and dicyanamide as follows:—Ten g. of the substance are put into a ½-litre flask; add 400 to 450 c.c. water, shake for two and a half hours and fill up to the mark. Put a quantity of the liquid corresponding to 0·2 g. of the sample into a 200 c.c. flask, acidulate with nitric acid, neutralize by 5 c.c. of 2½ per cent. liquor ammoniæ, add 50 c.c. decinormal silver nitrate solution, fill up to the mark, filter and estimate the silver in the filtrate. In the presence of chlorides, the solution must be acidulated with nitric acid and titrated for them. Dissolve 100 g. silver acetate in 400 c.c. 10 per cent. liquor ammoniæ, and dilute to 1 litre. Ten c.c. of this liquid is added to 25 c.c. of the lime-nitrogen solution prepared as above, filter and estimate the cyanamide by performing a nitrogen test according to Kjeldahl. To 25 c.c. of the filtrate (= 0·357 g. of the original substance) add 10 c.c. of 10 per cent. caustic-potash solution; the nitrogen contents of the precipitate indicates the dicyanamide. In order to estimate this directly, shake 10 g. of the sample with 250 c.c. 94 per cent. alcohol for half an hour, evaporate 100 c.c. of the filtrate on the water-bath, take up the residue with warm water, add 10 c.c. of the silver acetate solution, filter and wash the precipitate. To the filtrate add 10 c.c. of 10 per cent. potash solution, which precipitates argentic dicyandiamide; filter and estimate the nitrogen in the precipitate.

Vualflart (*Ann. Falsific.*, 1911, iv., p. 321) prepares the usual solution in a corked bottle, precipitates 100 c.c. (= 0·4 g. cyanamide) by 20 c.c. of a 5 per cent. silver nitrate solution and ammonia in excess, washes the precipitate, dissolves it in dilute nitric acid, and titrates with ammonium sulphocyanide, using ferric chloride as indicator. If the nitrogen of dicyanamide has to be estimated as well, the ammonia is replaced by 20 c.c. of a 10 per cent. solution of caustic potash, the precipitate is washed and dried, and the nitrogen estimated by the Kjeldahl method.

Ammonia and Cyanides prepared by Means of Titanium Cyanonitrid.

The Badische Anilin- und Sodafabrik (Fr. P. 387001) prepares cyanides and cyanamides from *titanium cyanonitride* by melting it with calcined sodium carbonate and lampblack, or by heating it with quicklime, calcium chloride, and lampblack. The titanium may afterwards be readily reconverted into the nitride or cyanonitride. Their Fr. P. 387002 shows that the nitrogen present in these titanium compounds may be readily converted into ammonia by most of the oxidizing agents, or by heating with acids in the presence of water or steam. The titanic acid formed in this process, when heated with carbon and salts of alkaline metals, absorbs nitrogen at a comparatively low temperature. Thus a mixture of 80 kg. titanic acid, 20 kg. wood-charcoal, and 2 kg. sodium sulphate requires heating in a current of nitrogen for two hours at about 1240° C.

The Ger. P. 200988 of the same firm treats of the preparation of cyanides and cyanamides of the alkalis and alkaline earths by heating the nitrogen compounds of titanium (the nitride and the carbon-nitrogen compound) with the oxides, carbonates, or other salts of the alkalis or alkaline earths in the presence of carbon, pitch of the like, with or without a flux. The titanic acid formed in this process can be reconverted into the nitride or carbon-nitrogen compound in the well-known manner.

The Ger. P. 202563 of the same firm produces ammonia from the cyanogen-nitrogen compound of titanium by heating this with oxidizing agents (apart from caustic alkali) at a suitable temperature, in neutral, alkaline, or acid solutions, suspensions, or in the state of fusion. Such agents are, *e.g.*, sulphuric acid and sodium bisulphate, together with water under pressure; or electrolysis, with or without oxygen carriers; or air, with water, with or without the assistance of high pressure and of oxygen carriers.

The Ger. P. 203748 of the same firm (to which corresponds the B. P. 1842, of 1908, taken out by Johnson for the B.A.S.-F.) describes a modification of the process of Ger. P. 202563. The titanium cyanonitride is soaked with a contact substance, *e.g.*, a solution of platinum chloride, and is then heated to 300° to 400° in a current of air and steam. Their Ger. P. 203750 describes the heating of titanic acid with coal in a current of nitrogen, after adding an alkaline salt (sulphate or carbonate), which enables the reaction to take place quickly and at comparatively low temperature. The alkaline salts seem to play the part of nitrogen carriers, since already small quantities produce a strikingly hastening action. Their G. P. 204204 protects the application of titanium nitride, Ti_2N_2, in lieu of the cyanonitride. Their Ger. P. 204475 shows that in this process steam may be employed as an oxidizing agent, if at the same time such metallic salts, oxides, or hydroxides are present, which under the circumstances of the case do not themselves oxidize the titanium nitrides.

Their Ger. P. 204847 describes the preparation of ammonia from titanium nitride by boiling this with sulphuric acid of 30 per cent., with exclusion of air. When employing concentrated sulphuric acid, the temperature must be kept below 170° C., to avoid the oxidizing action of the acid. The corresponding British patents taken out by J. V. Johnson, are 2414 and 2525, of 1908.

Formation of Ammonia from Nitrogen Oxides and in Various Inorganic Chemical Processes.

Atmospheric nitrogen, according to Schönbein, combines directly with the elements of water forming ammonium nitrite:

$$2N + 2H_2O = NH_4 . NO_2,$$

and this reaction occurs, although but to a minimal extent, every time when water evaporates in contact with air. Much more rapid is the combination of free nitrogen and hydrogen under the influence of the electric spark or of the silent electric discharge, but it is always very incomplete, since the contrary reaction by these agencies soon sets in. O. Loew (*Berl. Ber.*, 1890, p. 1443) has observed that atmospheric nitrogen is transformed by platinum black in the presence of caustic-soda solution into ammonium nitrite.

Ammonia is also formed when a mixture of hydrogen with "nitrous vapours," *i.e.*, various oxides of nitrogen, is passed through a gently heated tube filled with porous substances (preferably platinum sponge); cold platinum in such a mixture turns red-hot, and causes the combination of nitrogen and hydrogen with great violence. Hydrogen in the nascent state causes the formation of ammonia from nitric or nitrous acid; it is obtained in that state when being liberated by aluminium, zinc, or a mixture of zinc and iron. Ulsch (*Z. anal. Chem.*, xxx., p. 175) has shown that by means of iron alone, in a highly comminuted form ("ferrum reductum") and dilute sulphuric acid, nitric acid can be completely converted into ammonia; at 60° this reaction is complete, and it has been applied for many years to the quantitative estimation of nitrates. I myself have shown (Lunge, *Chem. Ind.*, 1883, p. 302; *J. Soc. Chem. Ind.*, 1884, p. 287) that in concentrated solution iron by itself, in the presence of caustic alkalies, reduces nitrates to ammonia. Sodium sulphide as well in the presence of sodium hydrate, on heating with nitrates, causes the formation of nitrates (Lunge and Smith, *Chem. Ind.*, 1883, p. 298).

Adhikary (*Chem. News*, cxii., p. 163, 1915) reduced nitric acid to ammonia by mixing it with hydrogen, and passing over heated Au, Ag, Zn, Sn, Pb, Sb, Bi, or Fe.

Boudoin and Escarpit (Fr. P. 205584) describe the production of ammonia by heating 100 parts sodium nitrate with 40 parts naphthalene to about 600°. In a similar way Fouler (Ger. Ps. 57254, 75610, 76724) treats nitrates with hydrocarbon to produce ammonia. These processes will certainly not yield quantitative results.

Angelucci (*J. Soc. Chem. Ind.*, 1907, p. 147, from *Gazz. Chim. Ital.*, 1906, p. 517) obtained ammonium carbonate from acetylene and nitric oxide by passing them through spongy platinum heated to 800° C.

Patten and Robinson (*Trans. Amer. Electrochem. Soc.*, Oct. 1907) have studied the conversion of nitric acid into ammonia by electrolysis. When employing a copper cathode, probably first hydroxylamine is formed.

The work done by Klut (*Mitt. d. Prüfungsanst f. Wasserversorgung*, 1909, part 12) and Noll (*Z. angew. Chem.*, 1910, p. 1307) on the formation of ammonia from nitrates in underground water, containing iron and manganese, is only theoretically interesting.

The Elektrochemische Werke, Berlin (B. P. 16426, 1911) produce ammonium nitrate by electrolyzing mixtures of nitrous and nitric acid in a diaphragm cell with an aluminium cathode.

The same firm (Ger. P. 238137) prepare ammonia or salts of it from nitrogen oxides and hydrogen, or mixtures of hydrogen with gases containing carbon monoxide or suitable hydrocarbons; by passing them at high temperatures over contact substances which contain only a moderate quantity of catalytically acting metals or metallic compounds. The surface of non-porous contact substances ought to be only partially covered with contact metals. The advantage of employing such weak contact substances had not been previously known. In order to obtain quantitative yields, definite temperatures must be kept, differing according to the nature of the contact metal and to the concentration. Strongly acting metals, such as platinum, must be employed at smaller concentrations, but at higher temperatures than less active metals, as copper, nickel, or iron.

Their Fr. P. 426307 (U.S. P. of Rothe, 1083703) states as the most suitable catalytic mass, asbestos impregnated with 10 per cent. copper.

In some other cases where nitrate of soda is used for oxidizing purposes, ammonia is formed, and proposals have been made for its utilization. This is, for instance, the case with the ammonia formed in very perceptible quantities during the oxidation of the sulphur compounds in the manufacture of caustic soda at first observed by Pauli,[1] and studied in detail by Lunge and Smith (*J. Soc. Chem. Ind.*, 1889, pp. 460 and 525). It would seem very difficult to recover this slight quantity of ammonia diluted with an enormous volume of other gases. But at the Aussig Chemical Works this is actually done; and already in 1884, 60 tons of ammonium sulphate were obtained from this source.

In "black-ash" obtained by the Leblanc process there is always a certain amount of cyanides, which cause a good deal of trouble in the manufacture of pure soda. Matthieson and Hawliczek have worked out a process (B. P. 5456, of 1886; Ger. P. 40987; *J. Soc. Chem. Ind*, 1889, p. 351) by which they transform the cyanide into ammonia by means of superheated steam at 300° to 500°. An account of this is given in Lunge's *Sulphuric Acid and Alkali*, 3rd edition, 1909, ii., p. 618. This process has never become practical; no more has this been the case with the process of Gorlich and Wichmann (Ger. P. 87135), who allow the H_2S, evolved in the Leblanc process or otherwise, to act upon sodium nitrite:

$$NaNO_2 + 3H_2S = NaOH + 3S + NH_3 + H_2O.$$

Tralls (Ger. P. 41352) recovers ammonia in the manufacture of sulphate of alumina from bituminous schist by adding a little gypsum before calcining the schist.

Kellner (B. P. 13722, of 1893) electrolyzes sodium nitrate in the following way:—A solution of sodium nitrate is electrolyzed with a mercury cathode, and the sodium amalgam formed is employed as cathode in a solution of sodium nitrate, into which dips a second electrode, in order to recover the electric current generated during the action of the Na on $NaNO_3$, in which NH_3 and NaOH are formed.

Raschen and Brock (B. Ps. 7287 and 7288, 1895) treat equal molecules of sodium nitrate and chloride with an excess of sulphuric acid; the nitrosyl chloride formed is mixed with hydrogen and is passed over hot platinum-asbestos, the reaction being:

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[1] *Phil. Mag.* [4], xxiii., p. 248.

$$NOCl + 6H = NH_4Cl + H_2O.$$

If NOCl is replaced by N or oxides of nitrogen, free NH_3 is formed.

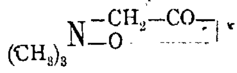
The West-Deutsche Thomasphosphatwerke (Ger. P. 157287) subject a mixture of hydrogen, nitric oxide, and carbon monoxide to the action of spongy platinum, at a temperature not exceeding 80° C. and aided by the silent electric discharge. In practice the mixture would be made of Dowson gas or water-gas and nitric oxide. A mixture of 12 vols. H, 40 NO, 44 CO, and 4 CO_2 yields on the average about 10 vols. NH_3.

Cassal (Fr. P. 346066) absorbs the gases produced by the action of an electric discharge on air, and consequently containing nitrogen oxides, in caustic alkali so as to form nitrates and nitrites, and electrolyzes the solution without a diaphragm. Ammonia is liberated as a gas, and the caustic alkali is re-formed. The yield is improved by addition of 5 per cent. of lead nitrate. Nitrites must be present, unless a small-current density is used at the cathode. Instead of caustic alkali, lime or calcium carbonate may be used as the absorbent.

Peacock (U.S. P. 1123584) produces ammonia by burning sulphur with a limited amount of air to deprive the air of nearly all its oxygen, bringing the resulting mixture of SO_2 and N into contact with carbon at a temperature of about 800°, to form $S_3N_4(C_3H_4)_2$ or $S_3N_4(C_3H_4)_3$, and treating the latter with hot water or steam to produce NH_3.

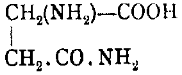
AMMONIA AS A BY-PRODUCT IN THE MANUFACTURE OF BEETROOT SUGAR (VINASSE).

Beetroot contains betaine (trimethyl-glycocol):



$$(CH_3)_3N\begin{matrix}-CH_2-CO-\\-O-\end{matrix}$$

also asparagin:



$$\begin{array}{l}CH_2(NH_2)-COOH\\|\\CH_2.CO.NH_2\end{array}$$

and other chemical compounds, from which, by decomposing reactions, ammonia (along with trimethylamine) is split off. This is facilitated by the addition of lime to the beetroot juice, for the purpose of purifying it; and, in fact, the juice, after this treatment, during its concentration constantly emits small quantities of ammonia. It has been several times proposed to recover this ammonia. Thus, Vibrans (Ger. P. 15513) aspirates the steam and ammonia collecting in the upper part of the "thick juice" evaporators by means of a pump, and passes it through an acid; he also treats in a similar way the ammonia given off in the "saturating-pans." Hudec (*Fischer's Jahresber.*, 1895, p. 817) obtained from 100 c.c. the condensed water of the evaporating-boilers 0·0432 g. NH_3. More can be got by spraying alum solution into the boilers, or, according to Polecke (Ger. P. 52885), gaseous or sprayed acids.

It is, however, much more important to recover the ammonia found in a more concentrated state in the "*vinasse*," that is the residue from subjecting the molasses to fermentation, and distilling off the alcohol. The best-known process is that of Cam. Vincent (*Comptes rend.*, 1877, 21 mai and 8 octobre), which has for its principal object the manufacture of trimethylamine and methylic chloride, but considerable quantities of ammonia are likewise obtained (about 32 cwt. of ammonium sulphate from 98 tons of molasses, or 400 tons of vinasse, treated per diem). The evaporated vinasse is ignited in retorts and the gases are submitted to condensation; the tarry liquid which separates is saturated by an acid and evaporated to a certain degree; on cooling, the ammonia salts, which are less soluble than the others, crystallize out. A further quantity of ammonia is obtained in the destructive distillation of the trimethylamine hydrochlorate, in a similar way to the above. The ammonium salt thus obtained (generally the hydrochlorate) is contaminated with the chlorides of iron and lead from the metal of the vessels; it is purified by dissolving in water, adding ammonium sulphide, filtering, crystallizing, and draining the crystals in a centrifugal machine.

E. Ernst (Ger. P. 13871) mixes with the vinasse, concentrated to 76° Tw. and still hot, 25 per cent. dried ground peat, 3 per cent. ground quicklime, and 6 per cent. fatty oil. The mixture is charged into a simicircular piece of sheet-iron, which is placed in a red-hot horizontal retort, iron rails preventing a direct contact between the sheet-iron and the retort-shell. The gases formed are treated as usual. Further patents of the same inventor (Ger. Ps. 17869 and 18549) describe other arrangements for igniting mixtures of vinasses with peat, etc.

R. Lederer and W. Gintl (Ger. P. 17874) calcine the concentrated vinasse in a continuous stream, at a temperature of 350° to 400° C., in a horizontal retort, filled with an Archimedian screw, so that the char continuously issues at the other end, ready for the recovery of potash salts, the gases being treated by Vincent's process, *supra*, p. 1149.

F. X. Brosche (Ger. P. 14433) states that 60 or 70 per cent. of the nitrogen of the vinasse can be recovered as ammonia by dry distillation of the vinasse over potash-lime, formed by a mixture of carbonized vinasse with lime. Up to 80 per cent. is obtained, if the vapours are, moreover, passed through a tube filled with potash-lime.

The Badische Gesellschaft für Zuckerfabrikation (Ger. P. 15702) extracts carbonized vinasse with water, causticizes the solution by lime, evaporates the liquor, and adds so much of it to concentrated vinasse that there is from 5 to 15 parts of potassium hydrate present for each 100 parts of dry vinasse. The dry distillation is then carried on as usual.

Haring, Ehrenberg, & Co., and M. Baswitz (Ger. P. 15751) introduce concentrated vinasse, or the liquors from the osmose and elution processes, in a very thin stream into retorts heated to a dark red-heat, so that there is almost instantaneous gasification. The gases, which are very rich in tarry matters, are subjected to overheating in pipes placed between the retorts, where the tar is destroyed [along with some of the ammonia ?], and thence pass into the condensing apparatus.

Even from the *potash* made from vinasse, which contains some potassium cyanide, Legrand and Dabernard (Fr. P., 27th December 1876), state that they can obtain ammonia by treating it with steam. Thus 1 to 4 per cent. ammonium sulphate is to be obtained from potash.

Emil Meyer (Ger. P. 43435) proposes working the liquor left on recovering sugar from molasses not merely for ammonia and alkali salts, but also for oxalic acid, by fusing the salts with caustic soda or potash; C. Uhl & Co. (Ger. P. 47190) propose improvements to this process. Sternberg (Ger. Ps. 78442 and 105638; U.S. P. 486647) evaporates the same liquor with coke and distils the mixture in retorts with superheated steam, which converts much more of the nitrogen into NH_3. The formation of ammonia commences at 100° C.; at 300° 50 per cent. of the nitrogen compounds are converted into NH_3, and at 500° the decomposition is practically complete. His apparatus is shown in Fig. 233. It consists of three superposed retorts, connected by vertical pipes and fitted with agitating-worms. a_1 is the charging-funnel, *d* the discharging-pipe. The fire-gases travel along A, B, C, D, E, F, and through G into the chimney. The material enters at a_1 and proceeds along a, a_2, a_3, into b, then along b_1, b_2, through c, c_1, into the cooler d, and is discharged by d_1 and d_2. d can be connected by e with a gas-pump, which serves for aspirating air from a_1 right through the retorts.

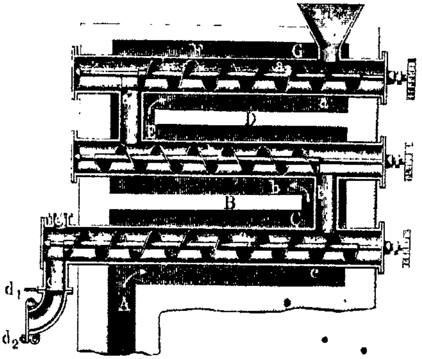


FIG. 233

H. & W. Pataky (Ger. P. 86400) mix the evaporated liquor with alumina and distil in retorts; the residue contains potassium aluminate, besides other salts.

Mathiessen (Ger. Ps. 89147 and 93397) also employs alumina in various forms for increasing the yield of ammonia from molasses.

In treating molasses with lime and alcohol, for the purpose of recovering the sugar, the alcohol distilled off from the calcium saccharate contains ammonia.

H. Steffens (Ger. Ps. 23594 and 24549) treats it with sulphuric, carbonic, sulphurous, or phosphoric acid, or acid salts, in order to recover the ammonia.

Effront (Fr. P. 369630, and Ger. P. 209114, of 1909) increases the yield of NH_3 from boiled-down vinasse by mixing it with resins or with acid salts, obtaining part of the NH_3 by drying the mixture in a current of hot air and distilling the residue at 700° C. in presence of superheated steam and of an excess of air. Another patent of the same inventor (Fr. P. 382689) employs butyric-acid ferment at 38° to 42° C. During the fermenting process, which lasts about three days, 15 to 20 litres of butyric acid are formed. An alkalinity of about 1·5 g. per litre must be maintained by the addition of lime.

Ost (*Z. angew. Chem.*, xix., p. 609) describes the utilization of vinasse by the process used at the Dessau works.

Sternberg (B. P. 7002, of 1896; Ger. P. 105638) mixes the sugary liquor with a crude potassium aluminate, obtained from bauxite, and heats the blocks thus made in a continuously acting retort.

Fischer (B. P. 15815, of 1899) heats thickened vinasse in a series of retorts, provided with alternately working screws to from 200° to 500° C.

Besemfelder (Ger. P. 118795; U.S. P. 689780) mixes the concentrated waste lyes of sugar-works with bauxite, or alumina and coke, and heats the mixture in a series of horizontal superposed pipes. The gases are conveyed into "decomposition-retorts," and the tar produced there, together with ammonia, is separated therefrom.

Andrlik (*Chem. Zeit.*, 1902, rep. p. 274) describes his experiments with the same material, especially the use of certain bacteria for converting the nitrogen into ammonia.

Further patents in this line are: Peceker Zuckerraffinerie (Aust. P. 1284); Indre and Thierry (Ger. Ps. 125788 and 129578; Aust. Ps. 5158, 5159, 6861, 8878); Wenck (Ger. P. 108724); Schiller (Ger. P. 38596); Huber and Poindexter (U.S. P. 1145484).

It is stated that, if all the German beetroot sugar works worked the vinasse for ammonia, about 15,000 tons of ammonium sulphate could be produced per annum, most of which is now lost. The more recent endeavours for utilizing the vinasse in this respect aim at obtaining the nitrogen in the shape of cyanide (*e.g.*, Reichhardt and Bueb, Ger. Ps. 86913, 87725, 104953, 113530), which seems to be more profitable.

The Deutsche Gold- und Silber-Scheideanstalt (Ger. P. 255440) obtain practically the whole of the nitrogen of the vinasse by superheating the gases, produced in heating the vinasse, in tubes of quartz or of a fused mixture of zirconia and quartz.

The Société H. Gouthière & Cie. and P. Ducancel (Ger. P. 270325) convert the methylamine, contained in the gases from the destructive distillation of vinasse, into ammonia by heating the gases to 500° to 700°.

According to the Fr. P. 442923 of the same inventors an intimate mixture of vinasse (concentrated to a pasty state) and a portion of the residue from a previous operation is submitted to destructive distillation in the presence of steam, so as to liberate most of the nitrogen present in the form of ammonia, which is converted into sulphate in the usual way. The combustible gases produced by the distillation serve to heat the retorts or ovens employed, and part of the residue is treated for the attraction of potassium salts. Additions to this patent extend the process to all residual liquors having a composition similar to vinasse (like the liquors from the scouring of wool and the mother liquors of sugar refining), and describe the recovery of glycerin and potash; also the conversion of the methylamines into ammonia, as in the above-quoted German patent.

Donath (*Oesterr. Chem. Zeit.*, 1915, p. 112) discusses the recovery of ammonia as a by-product in the manufacture of beetroot sugar. Various authors have worked on the occurrence or formation of ammonia in the treatment of the beetroot juice with lime. This ammonia is partly liberated from the ammonium salts present in the beetroot juice, partly formed from the protein substances and amido-compounds contained in the juice. According to the experiments made by Donath himself, from 0·1004 to 0·1643 g. NH_3 can be obtained from 1 kg. beetroot in the laboratory. Various patents have been taken for recovering the ammonia in actual practice, of which the Ger. P. 281095 of the Chemische Produktenfabrik Pommerensdorf and R. Siegler deserves special attention. They expose the gases or vapours to gases containing SO_2 or HCl, and obtain the ammonium sulphite or chloride formed from the concentrated aqueous solution formed by centrifugalling or otherwise. The sulphite is converted into sulphate by "autogeneous oxidation."

AMMONIA FROM URINE, SEWAGE, ETC.

Urine is no doubt the oldest source of ammoniacal compounds, and up to a comparatively recent period it was practically the only one for manufacturing purposes. The first chemist who really deserved that name, the Arabian Geber, who lived in the eighth century, undoubtedly prepared sal-ammoniac from urine and common salt. Sal-ammoniac, made in this way, was an article of commerce in Europe as early as 1410; and the Jesuit Sicard in 1720 describes a manufactory of it in the Delta of the Nile which he had visited. In Egypt sal-ammoniac was made by mixing camel's dung with salt, burning it, and collecting the sublimate; we shall give some more particulars concerning this subject in the section "Sal-ammoniac" in Chapter XVII.

Putrefied urine (in which the urea has passed over into ammonium carbonate) has been used for centuries, and to a certain extent is still used by dyers as a source of ammonia for scouring wool and other purposes.

The methodical collection of urine or sewage and working it up into ammoniacal compounds has been carried out in the neighbourhood of some large towns, *e.g.*, Paris; but this industry represents only a very small proportion of the enormous quantity of animal ejections passing off in other ways, and it furnishes only a comparatively small fraction of the ammoniacal compounds required in trade. If all the ammonia corresponding to London urine were recovered, this would amount to more than 60,000 tons of sulphate per annum.

Normal urine contains from 20 to 35 g. urea per litre: an adult man produces from 22 to 37 g. urea per twenty-four hours, along with $\frac{1}{30}$ to $\frac{1}{60}$ of that weight of uric acid; this corresponds to 12·5 to 21 g. NH_3 per day, or between 9 and 17 lb. per annum. Urine, left to itself, after a short time begins to ferment, the result being that urea, or carbamide, $CO(HN_2)_2$, takes up $2H_2O$ and is changed into ammonium carbonate, $(NH_4)_2CO_3$, under the influence of a microscopic fungus.

In Paris[1] there are daily 2200 cbm. (say, tons) of urine and night-soil taken out of the "fosses," partly disinfected by sulphate of iron or zinc, and are left to settle in large reservoirs, where the solid matters separate from the liquid sewage, forming 85 to 95 per cent., which is now called "eau vanne." In three or four weeks the fermentation is complete, the urea has vanished, and there is formed principally ammonium carbonate, along with sulphhydrate, sulphate, chloride, ammonio-magnesian phosphate, compound ammonias, and other substances of intensely disagreeable smell. There is always a considerable loss of nitrogen, partly as such, partly by the evaporation of ammonia, and partly by its oxidation into nitric acid. When the fermentation is complete, the clear "eau vanne" is drawn off from the muddy deposit, which is converted into manure, but always with much loss and causing a great nuisance.

Several processes have been introduced for treating this very disagreeable deposit, of which we will give an outline. The Bilange process, practised at Bondy, is applied to the whole of the sewage. This is mixed by mechanical agitators with an exactly measured quantity of chemicals, intended to promote a rapid settling, principally consisting of milk of lime of sp. gr. 1·16 to 1·20. The mixture is allowed to settle in tanks, holding 500 tons each. After an hour the clear liquid is pumped away; it has an amber colour and contains free ammonia. The albuminoid matters are precipitated along with carbonate of lime and most impurities. The decanted liquid is replaced by a fresh mixture from the agitators; the clear portion is again decanted, and this is continued until the tank is full of deposit. The thick mud is now heated by steam (it is more easily pressed when hot) and is passed through filter-presses. The ammonia escaping during the heating is retained in tanks filled with sulphuric acid. The cakes turned out from the filter-press are much richer in nitrogen the less lime has been used. Each 100 cbm. of crude sewage yield 75 cbm.

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[1] C. Vincent, "Industrie des Produits ammoniacaux," *Enc. Chim. Frémy*, 2nd ed., 10th vol., 4th part, p. 7.

clear decanted liquid and 25 cbm. deposited mud, from which is obtained 6 or 7 tons of cakes containing 50 per cent. moisture. The manurial value of the latter is very small. The liquid is worked up in the ammonia-stills.

The Kuentz process has been worked in several places, *e.g.*, at Versailles. The crude sewage is received in closed tanks, where it passes through zigzag channels, and thus undergoes a first settling. The clear liquid issuing at last is sent to the ammonia-stills. The thick deposit is pumped into a closed mixer, where it receives an addition of the chlorides of aluminium and iron and of phosphate of lime, in order to make it pass through the filter-press and enhance its manurial value. The reagent is prepared by treating a mixture of 15 parts bauxite, 75 parts natural phosphate of lime, and 3 parts hydrated oxide of iron (yellow hematite) with 110 commercial hydrochloric acid and 150 water. Fifty kg. (1 cwt.) of the liquid resulting from the reaction is added to each cubic metre of thick mud. After twenty-four hours' settling a considerable quantity of clear liquid, with only a faint smell, collects at the top and is decanted, and the deposit is forced by compressed air into a filter-press. The cakes contain all the phosphoric acid as bicalcic phosphate, precipitated by the ammonium carbonate, along with calcium carbonate; the iron has absorbed the sulphur compounds, and the alumina has modified the albuminous and slimy matters which otherwise would have impeded the filtration. The percentage of nitrogen in these cakes is 3 to 3·5, that of assimilable phosphoric acid 10 to 12 per cent.

The ammonia-stills must be specially adapted to avoid the smell inherent to such matters; they will be described in the last chapter.

It is hardly necessary to observe that all such processes apply only to concentrated night-soil, not to sewage diluted with a large quantity of water from water-closets, etc.

Ketjen (*Z. angew. Chem.*, 1891, p. 294) reports on a successful experiment, made at Amsterdam, for recovering most of the nitrogen of sewage by distillation with lime. The apparatus was similar to that employed in distilling gas-liquor, sufficient to work up 50 tons in twenty-four hours. The sewage contained 2·018 per cent. free and 0·326 " fixed " ammonia; only 0·00848 per cent. NH_3 remained in the waste-liquor. 8750 tons of sewage yielded 72 tons sulphate of ammonia, with the expenditure of 123 tons quicklime, 153 tons coal, and 72 tons sulphuric acid, sp. gr. 1·7. The fixed residue, mixed with lime and pressed in a filter-press, contained 58 per cent. dry substance, 52·27 per cent. $CaCO_3$, 0·518 per cent. N, 0·155 per cent. K_2O, and 0·157 per cent. P_2O_5. Neglecting its manurial value, the profit made on the sulphate of ammonia reduced the expense of dealing with the sewage to 44 cents. per ton of sewage, so that it was resolved to erect a plant for 250 tons per diem, in order to deal with the whole Amsterdam sewage.

Hempel (*Z. angew. Chem.*, 1915, i., p. 145) draws attention to the well-known fact that the sewage is everywhere treated in a very unsatisfactory way, and enormous quantities of it go away in the subsoil. Especially in large towns nearly all the human excretions are lost, since water-closets have been introduced all over. The employment of sewage for irrigating fields near the towns withdraws it from general use for the whole country. Kerner (quoted in Gorup-Besanez, *Physiol. Chem.*, 4th ed., p. 574) found in the urine of a man, who secreted on the average 1491 c.c. of urine per diem, 38·1 g. urea, 0·94 uric acid, 3·42 phosphoric acid, 0·38 calcium phosphate, 0·97 magnesium phosphate, 0·83 ammonia per diem. The human secretions amount on the average for one year and for one person to 0·43 cbm. urine and 0·083 cbm. fæces. The weight of a cubic metre of mixed urine and fæces is 958·8 kg., containing 0·14 to 0·19 potassa, 0·19 to 0·60 per cent. phosphoric acid, 0·41 to 0·35 per cent. nitrogen (most of it in the urine). If of the 1½ litres of urine, secreted per head, only ½ litre were collected, the 70 millions of people inhabiting Germany would furnish ammonia of the daily value of £32,500, or £11,850,000 per annum. This is, however, an illusory demand; under ordinary circumstances it will be preferred to supply the nitrogen for agricultural purposes in the shape of "lime-nitrogen" (*vide supra*, pp. 1137 *et seq.*), or by synthesis of ammonia by the process of Haber (p. 1070) and other processes of that kind. An electric plant of 5000 kilowatt produces per annum 2500 tons nitrogen in the shape of "lime-nitrogen," corresponding to 11,800 tons sulphate of ammonia, and to the nitrogen of the urine of 283,966 adult persons. Hempel also studied the question of converting the nitrogen of urine by fermentation into urea. At a temperature of 30°, and adding to a litre of fresh urine 50 c.c. of fermented urine, the urea was completely converted into ammonium carbonate within forty-eight hours. The evaporation of urine, treated in this way, had, however, the disagreeable accompaniment of violent frothing and most disagreeable smell. The evaporation of fermented urine causes great losses of ammonia, which are only partly avoided by the recommended addition of calcium sulphate; but fresh urine can be easily concentrated to a tenth of the original volume by evaporation in iron pans, heated by waste fire-gases of some technical operations, *e.g.*, the manufacture of coal-gas.

We will now enumerate various patents referring to this subject.

J. P. Rickman and J. B. Thompson (B. P. 3305, 1882) add to urine and night-soil putrefying ox-gall as a ferment. The upper space of the closed tank in which the mass is kept is connected with a reservoir containing sulphuric acid, to absorb the ammonia escaping. The liquid remaining in the fermenting-tank is afterwards distilled at a low temperature; the vapours from the directly heated still first pass through liquid contained in a cold still and thence into the absorbing-vessels.

J. Young (B. P. 3562, 1882; Ger. P. 27034) distils off a portion of the sewage, or of the effluent waters of sugar manufactories, either by itself or mixed with lime, at a pressure above or at or below that of the atmosphere; the distillate contains a greater proportion of ammonia than the original sewage. His apparatus consists of a series of long boxes, arranged like steps, and provided with false bottoms inclined in such a way that when the boxes are filled with the liquid, which is previously warmed and mixed with lime, the steam which is admitted at the bottom can be sucked by means of a vacuum backwards and forwards through the whole battery of boxes, while fresh liquid flows continuously in at the top and out at the bottom. Instead of the boxes, cylinders may also be employed.

J. Duncan (Ger. Ps. 27148 and 28436) treats sewage, mixed with lime and cleared by settling, with steam in such a manner that the boiling-point 50° C. is never exceeded. This is done by means of a series of vessels combined into a battery, in which the liquid travels in the opposite way to the steam. When the liquid contains only about 0·5 g. NH_3 per litre, steam takes up hardly more than $\frac{1}{800}$ of its weight of NH_3 in a vacuum in which water boils at 21° C. It is therefore best to take the ammonia out of the steam by sulphuric acid, and employ the "purified" steam over again (?).

F. J. Bolton and J. A. Wanklyn (Ger. P. 17386) pass the vapours from heated sewage, etc., mixed with air or carbonic acid, through layers of porous calcium sulphate, mixed or not with calcium and iron phosphate, of calcium chloride, of its double salts with potassium or sodium chloride, or of potassium-magnesium chloride. The ammonium carbonate is transformed by those reagents into calcium carbonate and ammonium sulphate or chloride. When the reaction has gone far enough the mixture is heated, whereupon the inverse reaction takes place; ammonium carbonate escapes [of course in a dissociated form], and the original salts remain to be used over again.

C. H. Schneider (Ger. Ps. 27671 and 32890) promotes the natural settling of sewage by the addition of calcium chloride, whereby the ammonia is converted into a non-volatilizing compound; the slimy matters are also precipitated, and with old sewage a clear liquid is obtained which is easily decanted. With fresh sewage a further clarification by aluminium sulphate is advisable.

Richters and Hagen (Ger. P. 14210) force air into the mixture of sewage or night-soil with lime, by means of perforated pipes, and condense the ammonia in coke-scrubbers by sulphuric acid.

Brullé and Leclerc (B. P. 1086, 1880) run the sewage, etc., in thin layers over heated surfaces, and cause a current of air, passed over those surfaces, to carry away the ammonia.

I. van Ruymbecke (U.S. P. 342237, of 1886) aims at submitting liquids containing organic substances to a rapid putrefying process, by allowing them to act in the shape of a spray on substances impregnated with putrefaction-ferments in the presence of a strong current of air, so that air, ferment, and liquid are brought into intimate contact. The escaping air is deprived of its ammonia by treatment with sulphuric acid, and the residual liquid is also treated for ammonia as usual.

Buhl and Keller (Ger. P. 27671) precipitate the phosphates with lime salts and crude manganese chloride (still-liquors from the manufacture of chlorine); the settled liquor is distilled for ammonia. In lieu of manganese chloride, aluminium or zinc sulphate may be employed, say, from 4 to 16 kg. zinc sulphate to a ton of sewage, according to its consistency. This causes a kind of curdling, by which the liquids can be easily separated from the solids.' The latter are filter-pressed and dried, yielding 1 to 1½ cwt. per ton of sewage, with 2·6 to 3·5 per cent. N and 5·5 to 6·3 per cent. phosphate of lime. The filtered liquid is distilled with lime, and yields 75 per cent. of the NH_3 present in the sewage.

Wedemeyer's process for recovering NH_3 from sewage (Ger. P. 87591) and Bruch's process (Ger. P. 79486) can be only mentioned here.

On boiling fibrous matters (for paper or pasteboard) with lime at 8 atmospheres' pressure, about half of the N present is given off as NH_3. But according to Nast (Ger. P. 40980) all the nitrogen is transformed into NH_3, if besides 5 per cent. lime, 2 per cent. NaCl is added (?).

Schilling and Kremer (B. Ps. 15752, 1903; 14966, 1904; Aust. P. 20602) allow the sewage to stand for some time in coke or slag filters, let it run off, and pass hot gases, especially those produced in burning the mud collected on the gravel filters, through the empty filters, taking the gases to ammonia absorbers and thus obtaining the NH_3 retained by the filters, as well as destroying the substances which stop up the filters.

The Gesellschaft für Abwasserklärung, Berlin (Ger. P. 161166) separates the muddy deposits from the clear sewage and burns it, passing the gases through the clear portion of the sewage during the filtration, and from these by means of a fan-blast into an observer for ammonia.

Twynam, Egham, and Matthews (B. P. 2625, 1895) filter the sewage through a mixture of ferric hydroxide and phosphates, or a hydrated phosphoric iron ore, and afterwards expel the absorbed NH_3 by steam, or use the mixture directly as a fertilizer.

Naylor (B. P. 17650, 1902) mixes the refuse with lime and passes it through a chamber into which air, heated by the hot flue gases leaving the destructor furnace, is forced. The NH_3 is condensed as usual.

Butterfield and Watson (B. P. 19502, 1905) distil the pressed sewage sludge by means of heat and steam in vertical retorts with continuous action by means of the heat produced by the waste gases.

J. Jean & Cie. (Fr. P. 372171) pass the sewage on to a quickly rotating fan, thus producing a dense mist, which is passed through baffle-plates on which the water condenses; the air is then brought into contact with an acid to retain the ammonia.

Börner obtained a Fr. P. 290035 for recovering the ammonia formed in putrefaction processes.

Stauber and Kochan (Fr. P. 464227) avoid, in furnaces for obtaining ammonia from sewage sludge, peat, bitumen, etc., the decomposition of ammonia vapours above 500°, by separating the furnace into two compartments, *e.g.* by means of tubes, in one of which a flameless combustion takes place, whilst in the other the gas is evolved by heating, aided by the injection of steam.

The Soc. An. La Suburbaine (Fr. P. 454498) pulverizes the night-soil, together with milk of lime, by a turbine, bringing a strong current of air into contact with the spray, passing on the air laden with ammonia to a chamber where it is washed by an acid spray. This may be repeated in two or more chambers, the same current of air being drawn through them in succession. Their B. P. is 4687, of 1913.

Taylor and Walker (U.S. P. 603668) employ a vertical retort, with injection of steam under the grate.

Matthiessen (Ger. P. 89147) passes volatile organic compounds of any sort over a red-hot contact substance consisting of an alkaline or earthy aluminate.

Fryklind (B. P. 20241, 1904; U.S. P. 918744) distils the excrements with lime into sulphuric acid, contained in a closed vessel, and utilizes the steam produced in the latter for the primary distillation.

AMMONIA FROM GUANO.

Apart from the deposits of ammonium bicarbonate sometimes found in Peruvian guano (p. 1050), it is possible to extract considerable quantities of ammonia from guano by heating it with lime. This process was patented by Young in 1841; but it cannot be remunerative, since the direct manurial value of guano is superior to that of the ammonia salts obtainable therefrom. This is best proved by the proposal of Bunte and Grahn (Ger. P. 47601) to increase the ammonia present in guano or superphosphates by passing the ammonia obtained from gas-liquor directly into superphosphate. For 20,000 cbm. gas 1 cbm. superphosphate, with 18 or 19 per cent. soluble phosphoric acid, is employed. The superphosphate is thus used twice over, until 7 or 8 per cent. N are accumulated in it. According to Ries (*Fischer's Jahresber.*, 1888, p. 91) this process has done excellent service at the Munich gas-works.

AMMONIA BY CARBONIZING BONES, HORN, LEATHER, WOOL, HAIR, AND OTHER ANIMAL SUBSTANCES.

The carbonization of *bones* is carried out on a large scale for the manufacture of bone-charcoal, a substance very largely used in sugar manufactories and for several other purposes. In Germany and France this was formerly generally done by heating the bones in iron pots, one on top of another, which are placed in large numbers in a furnace, heated by a fireplace built on one side of it. Thus the gases proceeding from the fireplace get mixed with those escaping from the carbonizing bones, and the ammonia contained in the latter is too dilute to be condensed; but there is also too little of it to begin with, as the temperature in this case is very high and most of the ammonia is destroyed.

In England and Scotland, and nowadays also mostly on the Continent, bone-charcoal is generally made by heating the bones in iron or fireclay retorts, provided with condensing-apparatus similar to that of gas-works. In these a kind of tar, called "Dippel's oil," and some ammoniacal liquor are collected. This tar consists to a great extent of pyridine derivatives, and is partly worked for these. The ammoniacal liquor is worked up exactly like that of the ordinary gas-works; it is probably more contaminated than the latter with pyridine bases.

The proportion of ammonia formed in this case is much larger than when charring the bones in pots, as in the former process the gases are subjected to cooling immediately after leaving the retorts, while in the latter they are exposed to the full heat of the fire-gases, and the ammonia is thus decomposed. Moreover, the temperature attained in the retorts is lower than that in the pots, which is precisely the reason why many Continental manufacturers prefer the latter system, as the bone-char is of better quality.

The bones intended to be charred must be first freed from fleshy particles, etc., by steeping in water (preferably tepid) for twenty-four hours, and mechanical cleaning; they are then roughly broken up by fluted rollers and are submitted to the process of removing the grease. This formerly always consisted in boiling them in water, preferably in a butt or pan, heated by a steam-coil, in which the bones were suspended in wire-work baskets; after a few hours' boiling, all the grease was found floating on the top and was carefully ladled off, after which the baskets holding the bones were lifted out, thoroughly washed, and at last dried by prolonged exposure to the air. Several processes have been introduced for removing the grease by washing with disulphide of carbon, benzoline, and the like, in specially constructed closed apparatus, which admit of recovering the solvent, but which cannot be described here.

The dry bones are sometimes at once submitted to the charring process, especially when this takes place in retorts; but where they are to be charred in pots, the bones are usually first broken up by studded or fluted rollers, and the pieces sorted by machinery, so that the different sizes required by the consumers of bone-char are obtained beforehand. The smaller particles, which are of very little value as char, are ground up into bone-dust for manure; the larger pieces are separately charred.

The retorts for charring bones are sometimes horizontal, of a section similar to gas-retorts, and are fired in the same way; sometimes they are perpendicular, in which case they can be worked continuously, part of the contents being from time to time withdrawn at the bottom, and cooled without contact with air, while fresh bones are being introduced at the top. The gases are conveyed away by a lateral tube near the top, and are first passed through a hydraulic main, or some similar apparatus, where they have first to traverse a shallow layer of water; they then pass through a cooling-apparatus, which may consist of a series of upright metal pipes, connected alternately at top and bottom, and cooled by air or by a water-spray, and afterwards through an ordinary scrubber. The remaining gases, which still possess a very disagreeable smell, are conveyed back into the retort-fire and are there burnt. Care must be taken to introduce them in a very hot place, so that the combustion may be complete. Of course it is preferable to promote the passage of the gases by an injector or exhauster.

The condensing liquids are allowed to settle in tanks where the tar (Dippel's oil) is separated; it amounts to 1·7 to 2 per cent. of the weight of the bones, and unless it is worked for pyridine, etc., it is mostly burned as fuel under the retorts. The ammoniacal liquor is worked up like gas-liquor, as will be shown in Chapter XIV.; it generally yields from 6 to 7 per cent. of ammonium sulphate of the weight of the bones, of somewhat inferior quality and strongly coloured. (If all the nitrogen contained in the bones were converted into ammonia, this would amount to 20 or 25 per cent. of sulphate.)

A process sometimes followed in France consists in filtering the crude ammoniacal liquor through a layer of plaster of Paris (sulphate of lime); the ammonium carbonate is thus transformed into sulphate, which is recovered by evaporation, insoluble carbonate of lime remaining on the filter.

H. P. Lorenzen (Ger. P. 9989) passes the gases evolved in charring bones over red-hot lime, where the tarry matters are burned, and condenses the ammonia in coke-scrubbers charged with dilute sulphuric acid.

H. J. and E. B. Castner (B. P. 4057, 1882) also carry the products of the continuous distillation of bones, along with air, through heated tubes, thence over hydrate of lime, and, after cooling, into sulphuric acid. [The addition of air and subsequent heating would tend to destroy much ammonia.]

A material similar to the tar from bones, etc., is the "*acid tar*" of the Scotch mineral-oil works. From this tar, which contains a considerable quantity of pyridine bases, Redwood (*J. Soc. Chem. Ind.*, 1891, p. 108) obtains ammonia by neutralizing the acid with lime and distilling with superheated steam, thus producing a neutral tar and 21 per cent. of the nitrogen present in the shape of NH_3.

Other animal refuse (wool, hair, skin, horns, feathers, sponges, leather, and so forth) is principally employed for two purposes, namely, for manufacturing prussiate of potash and for manure. In the former case the refuse matter is sometimes charged directly, or after being simply dried, into melted carbonate of potash, and in this instance of course no ammonia can be recovered. But sometimes the animal matters are first charred in retorts, exactly as has been described for charring bones, and the ammonia formed is recovered in the same way. It has been found that the charred matters yield the same quantity of cyanogen compounds as if they had been employed in the raw state, that is at most one-fifth of the quantity corresponding to their percentage of nitrogen (say 10 to 15 per cent.). Hence all the ammonia recovered in the charring process would seem to be a clear gain; but in spite of this not much is made in that way, as the expense of charring in retorts in any case swallows up most of the profit. One thousand parts of horn on carbonizing furnishes, according to Dumas, 500 parts of ammoniacal liquor of 8° to 10° Tw. and 160 parts of Dippel's oil. Some of the ammonia can be obtained as a solid sublimate of crude ammonium carbonate.

The utilization of these refuse animal matters for manurial purposes is effected in different ways. Sometimes they are exposed to the action of steam in closed cylinders, whereby they become friable, and are then ground up and mixed with superphosphate, etc. Sometimes they are added without any preparation to manures otherwise prepared, but in this case they disintegrate in the soil with extreme slowness. The most successful treatment of these substances seems to be: dissolving them in hot concentrated sulphuric acid (which can be performed in cast-iron vessels), and utilizing that acid for manufacturing superphosphate. In this instance most, if not all, the nitrogen is converted into ammonia, as is done in Kjeldahl's analytical process for determining the percentage of nitrogen. But this ammonia is, of course, never separated in the free state or in the shape of a salt, being at once incorporated with the other parts forming the chemical manure.

Another process admits of recovering the ammonia as such, and is also, as it were, based upon an extremely well-known analytical process, namely, the estimation of nitrogen by soda-lime. L'Hôte treats the refuse matters with a 10 per cent.

solution of caustic soda, in the cold or at such a moderate temperature that no ammonia is set free. The substances are thus converted into a pulp or completely dissolved. This pulp or liquid is mixed with slaked lime and the solid mass is charged into cast-iron retorts, where it is heated at first only gently, to avoid a destruction of ammonia, afterwards to a red-heat. The ammonia contained in the escaping gases is condensed by means of sulphuric acid. The residue is composed of sodium carbonate and lime, and when treated with water the caustic soda is regenerated (no doubt only imperfectly), and can be used over again.

H. Proschwitzky (Ger. P. 10957) charges retorts with alternate layers of 1 part of refuse leather and 4 parts of lime. The gases evolved by heating are first passed through condensing-apparatus for separating tar, ammoniacal liquor, and crude ammonium carbonate, and thence into sulphuric acid. The remaining mixture of charred leather and lime is to be used as manure. The uncondensed gases are used for heating the retorts.

Th. Richters (Ger. P. 13594) soaks leather, blood, wool, hair, and other animal refuse with a solution of carbonate of potash, dries the mass, and heats it in retorts, not quite up to fusion. The volatile products (ammonia, tar, and gas) are treated in the usual manner. The residue contains potassium cyanide, cyanate, sulphocyanide, carbonate, hydrate, sulphide, and carbon. It is lixiviated with water in the presence of metallic iron or ferric hydroxide; thus the potassium cyanide is converted into ferrocyanide (prussiate of potash), which is recovered by crystallization; the mother liquor is used again for treating animal matters, and the caustic potash contained therein is converted into carbonate by admitting carbonic acid during the drying process.

An altogether similar process for the simultaneous manufacture of prussiate of potash and ammonia was tried as early as 1860-62, by myself, in company with another chemist, on a practical scale, and some tons of both products were manufactured; but the process was given up on account of the difficulty of preventing the mass from fusing in the retorts, which made its discharge a very awkward operation and rapidly destroyed the retorts. It is, however, possible that these technical difficulties might be overcome. The ammonia is, of course, quite a secondary product in this case, the value of the prussiate of potash being far greater.

W. H. Marriott (B. P. 4369, 1881) distils animal refuse in a kiln by introducing at the bottom a mixture of producer-gas and the exact quantity of air necessary for burning it.

De Bonardi (B. P. 29009, 1896) passes city garbage through a continuously working incinerating-furnace.

The experiments made by Mond (*J. Soc. Chem. Ind.*, 1889, p. 505) for recovering ammonia from refuse leather, with or without lime, did not yield any satisfactory results.

From "Seeschlick," *i.e.*, deposits containing a great deal of organic matter and probably of marine origin, found in large quantities near Stettin, the Deutsche Ammoniakwerke recover ammonia by destructive distillation, preferably in the moist state (Ger. P 115462). In Ger. P. 142505 they describe a furnace specially constructed for that purpose. According to Knublauch (Ger. P. 137453) the yield of ammonia is greatly improved if the "Seeschlick" is mixed with coal previous to the distillation.

P. O. Rowlands (B. P. 7740, of 1912) treats wool waste, shoddy, or the like, with a 5 per cent. solution of caustic soda, heated to about 100°, and subjects it to the action of an electric current having a density of 25 amps. per square foot, whereby ammonia is freely evolved at the cathode.

A. T. Smith (B. P. 5348, of 1913) mixes waste leather with coal, slack, or coke, and limestone or lime, and treats it in a gas producer with a mixture of air and steam. About 70 per cent. of the nitrogen contained in the leather is evolved as ammonia, which is condensed in the usual way, combustible gas being utilized in any desired manner.

Schreiber (Ger. P. 257188) produces ammonia from organic substances containing nitrogen by causing them to act at about 200° on masses containing hydrated iron oxides, whereby most of the nitrogen is converted into ammonia. In this way 80 per cent. of the nitrogen of pyridine and cyanogen compounds can be obtained as ammonia.

Stauber and Kochan (Fr. P. 464227) obtain ammonia from "back-water slime," peat, bitumen, etc., by dry distillation above 500°, preventing the decomposition of the ammonia vapours by dividing the furnace by water tubes into two *compartments, in one of which a flameless combustion proceeds, and in the other the gasification is effected by ignition, enhanced by steam.*

AMMONIA FROM PEAT.

Several of the processes for obtaining ammonia, described in the preceding sections, employ peat as an auxiliary, together with other materials. In this section we treat of the recovery of ammonia from peat where this is the principal substance.

The importance of utilizing peat more than has been done in the past, also in the direction of turning its nitrogen to account, follows from the vast surface of land covered by it. Prussia alone possesses about 6 million acres of peat land; the vast extent of this in Ireland is well known. Russia, Sweden, Norway, Holland possess vast peat lands; so does North America.

Peat contains a very considerable quantity of nitrogenous compounds, most of it probably already in the form of ammonium salts, partly formed by the decomposition of organic matter, and partly absorbed from the atmosphere. The nitrogen found in it varies from 1 to 2·5 per cent., and sometimes amounts to 4 per cent.; by destructive distillation the best descriptions of peat yield up to 8 per cent. by weight of ammonium sulphate; even inferior qualities yield about half that amount.

America possesses a vast extent of peat lands, especially on the Canadian frontier, at the east coast, in the low lands of the Mississippi, and on the states on the Gulf of Mexico; altogether about 140,000 square miles, and on an average 9 ft. deep. The peat contained therein is believed to amount to 13,000 millions of tons, from which on working it up for power gas, 640 million tons sulphate of ammonia might be got as a by-product. Even more extended are the peat lands in Alaska, of a depth of 15 to 20 ft. in the south-west, and 30 to 40 ft. in the centre and the north. Up to now nothing of this is utilized, but we perceive what enormous supplies may be got therefrom in the future.

According to researches made by Chuard (*Comptes rend.*, cxiv., p. 181), the soil on the top of peat-bogs, which is distinctly acid, acts in a strongly nitrifying way, producing in three months

0·020 per cent., in six months 0·062 per cent., in twelve months 0·298 per cent. N_2O_5. Calcium carbonate here seems to have rather an injurious action. It is uncertain whether the nitrifying process in this case is identical with that going on in ordinary soils.

The destructive distillation of peat yields a tar very rich in phenols, acetic acid, and paraffin, and it has been worked for the latter products in some parts of Germany and France, but is now probably quite superseded for this purpose by richer materials, as bituminous lignite, shale, etc. The cessation of this industry involved also that of the recovery of ammonia by the same process.

Sometimes peat has been treated in specially constructed gas-producers, where the ammonia is washed out from the gas before using the latter for heating purposes. Such a "gazogène distillateur," constructed by Lencauchez, is described and figured in C. Vincent's *Industrie des Produits ammoniacaux*, p. 82; but the recovery of ammonia in this case must proceed on the same lines as that proposed for gas-producers in general (see later on), and is equally unremunerative in most instances.

H. Grouven has made a special study of the recovery of ammonia from peat, especially that obtained from certain kinds of moor-lands ("Bruchmoore" and "Grünlandmoore"), which sometimes contains up to 3·8 per cent. N. The principle of Grouven's process (Ger. Ps. 2709, 13718, 18051) is, mixing the damp peat with chalk (in order to fix the sulphur), heating this mixture in upright cylinders by means of the gases remaining from the subsequent stages of the process, and passing the gaseous products of this destructive distillation through a "contact substance," consisting of peat, chalk, and clay in equal proportions, moulded into the shape of drain-tiles, and heated in upright cylinders to a proper temperature. Here the nitrogen, under the influence of the incandescent aqueous vapour, hydrocarbons, and hydrogen given off in the first cylinders, is, to a great extent, converted into ammonium carbonate, which is condensed by calcium sulphate and thus converted into ammonium sulphate, or else by strontium sulphate (Ger. P. 34086).

Grouven's process was taken up by a company, and prolonged experiments on a large scale were made with it, but without pecuniary success, in spite of the then high price of ammonia. The question of utilizing the very large quantity of nitrogen contained in peat is therefore not yet finally solved, as it would not stand competition with the processes where ammonia is a by-product.

Rüderer, Loé, and Gumbart (Ger. P. 53844) combine the recovery of ammonia and acetic acid from peat with that of charcoal, but offer no peculiarity in the treatment for ammonia.

According to Kuntze (Ger. P. 62589), on distilling peat, part of the nitrogen escapes as nitrates and pyrrol, and pyridine bases, amines, etc.; later on as ammonium cyanide and very little ammonia. A considerable formation of ammonia is attained only by superheating with steam on a large surface of hot, porous material containing much lime. Even then most of the nitrogen remains in the coke, and is convertible into ammonia by superheated air, saturated with steam. This he effects in the apparatus shown in Figs. 234 and 235. A is the distilling-chamber, *k* flues for heating this; *g* a number of bell-shaped cast-iron vessels which allow the vapours, but not the solid matter, to penetrate into the centre of the retorts. The partition *a* divides the upper drying space from the lower distilling space. The steam produced in the former escapes by S, the vapours from the latter by B. The peat, after having passed through the retort and been converted into coke, is conveyed through W into the gas-producer G, where the coke is gasified by means of superheated, moist air. The vapours formed in A are aspirated through B into a retort, C, filled with porous tar-coke, containing lime and kept at red-heat. The tar, ammonia, and vapours formed here deposit part of the tar in the hydraulic main D, the other tar and some ammonia in the water-scrubber E, the rest of the ammonia in the acid-washer E^1, and the volatile hydrocarbons in the oil-scrubber F; the remaining gases are forced through X into the retort fires. The gas-producer G furnishes gas rich in NH_3, which is carried away by the flue H, serves for heating air in L, and is conveyed into chamber K, in which water is splashed about by paddles. Here the gas is cooled down to 100° C. and leaves dust behind, containing a little ammonia, whilst the bulk of the ammonia is recovered in the sulphuric-acid scrubber Q. The gases are deprived of most of the steam contained therein by cooling down to 30° C. by a spray of cold water in scrubber R, and are now sufficiently dry to be blown through O into the fire by means of blower *y*. The water from R, which is at a temperature of about 80 C., is pumped on to another scrubber T, into which air is forced by blower Z, and is thus reduced to 70° or 80° and saturated with moisture. The water thus cooled returns to R; the moist current of air is superheated to 200° or 300° and blown through M on to the step-grate N, where it unites with the superheated steam from A, aspirated through S. The worm U constantly removes the ashes from the producer G, in proportion as the coke is burned. The angle of the step-grate N is sufficiently steep for the coke to sink down continuously from A.

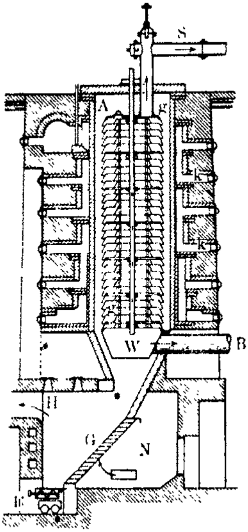

FIG. 234.

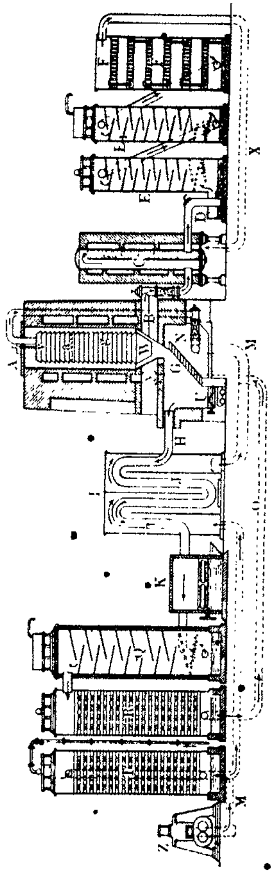

FIG. 235.

Pieper (Ger. P. 87061) first dries and slightly distils the peat in a revolving retort and then heats this to a very low red-heat, with introduction of steam. This produces CO_2, H_2, and NH_3. The NH_3 is absorbed by sulphuric acid, the remaining gas serves for heating. Later on, Pieper, together with Fellner and Ziegler, improved this process (Ger. P. 93705) by separately treating the gases from the distilling and steaming stages. After the first distillation the gases, containing two-thirds of all the ammonia, are by means of a valve conveyed into another channel; they are passed through a scrubber and contain merely H_2, CO, CO_2, and NH_3, so that they can be at once worked for pure ammonia preparations, whilst the gases from the first stage contain too much tar and must be treated in a more complicated manner.

Fig. 236 shows the furnace used for the above process. The cylindrical retort A revolves in furnace B; C, inlet for steam; D, outlet for gases; 1, 2, stuffing-boxes; 7, 7, flanges resting on rollers 8, 8, turned by the cog-wheel 9; 10, carrying-worm, working in the case 11. If the retort is turned 180° from the position shown in the figure, neck 12 connects with the charging-funnel E. As shown in the figure, the retort is discharged into the carrier F. The heating takes place by gas, entering through H and *h* into the mixing and inflaming chambers N and b_2, together with heated air through G. The mixture travels through b_3 and b_4 into chamber *b*; the fire-gases travel through b_6 and b_6 before escaping through b_7, where the heating of the air takes place. The steam-pipe C is connected by *i* with pipe J, for superheating it. The outlet D can be connected by *k*, *l*, *m* with the pipes K, for steam (during the drying stage), L for gases of the distilling stage, M for the mixture of water-gas and ammonia during the last stage. A number of such retorts can be systematically connected.

An English patent of Pieper's (B. P. 28190, 1896) prescribes a series of six retorts, connected with one another for continuous working by means of steam superheated to 500° C.

M. Ziegler describes another furnace for gasifying peat with recovery of the by-products in Ger. Ps. 101482, 103507, and 145374 (*Z. angew. Chem.*, 1899, p. 204). It is a perpendicular oval retort, the lower part of which is made of fireclay, the upper part of cast-iron, heated from the outside, and coking 10 to 12 tons air-dried peat in twenty-four hours. The uncondensed gases suffice not merely for heating the retorts, but also for the steam boilers, for lighting the works, and for driving gas-motors. Glinzer (*ibid.*, 1901, p. 862) gives a very favourable report of the work done by Ziegler's furnace at Redkino, in Russia, where by working up the tar and the aqueous distillate there is obtained from the peat 2 per cent. gas-oil, 0·5 per cent. creosote, 0·4 per cent. paraffin, 0·4 per cent. methyl alcohol, 0·8 per cent. ammonium sulphate, and 1·2 per cent. acetate of lime.

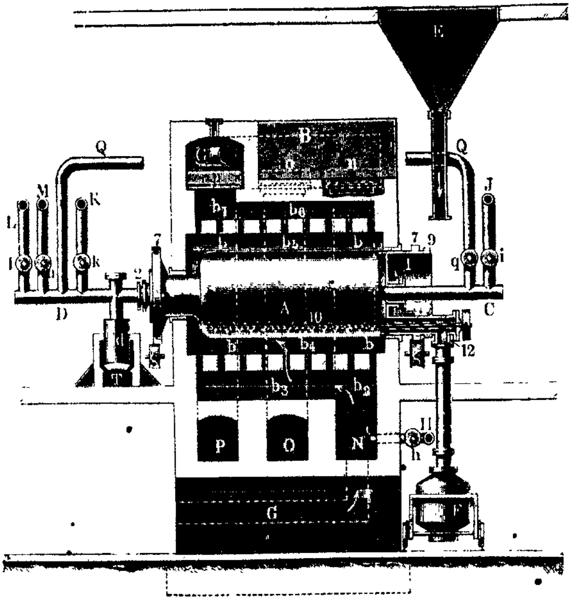

FIG. 236.

Woltereck obtained a B. P. 16504, of 1904, for the production of ammonia from peat by means of passing air and steam over or through it at a carefully regulated temperature. An improvement on this is his process (B. Ps. 28963 and 28964, of 1906), which provides for retaining the tar formed in the process, and which has an injurious effect on the quality of the produced acetate of lime and sulphate of ammonia, by passing the hot gases through a scrubber containing hot paraffin oil of a boiling-point about 300°, whereby the bulk of the tar is removed without simultaneous condensation of the water. The temperature of the peat is to be kept at 350° to 400°, not above this, to avoid a splitting up of the ammonia. In order to regulate the temperature, Woltereck and the Sulphate of Ammonia Co. (B. P. 27905, of 1908) pass a portion of the gas remaining after the removal of the ammonia, which contains much aqueous vapour, into the furnace or gas-producer below the zone of reaction, where it gets mixed with the air introduced for carrying on the process. According to their B. P. 15285, of 1910, they pass a mixture of steam and a portion of the waste gases over the heated peat, taking care that the gaseous mixtures do not contain enough oxygen to form combustible gases. The temperature thereby rises to 600° to 800°.

We have seen *supra* (p. 1068) that Woltereck, apart from the nitrogen of peat, wishes to produce ammonia also from the nitrogen of air, which is to combine by contact action with the hydrogen formed in his process.

Woltereck carried on an experimental plant for his process at Willesden, near London, during two years. Then the Sulphate of Ammonia Co. took over his process, and proceeded to erect a larger plant in Ireland. In *Chem. Trade J.*, xlii., p. 143 (1908), it is stated that works for carrying out the Woltereck process were then in course of erection in the north of Ireland, near Carnlough Harbour, for an annual output of at least 5000 tons of sulphate of ammonia by that process. In trials on the large scale work had been continuously carried on for several weeks; 585 tons of moist peat (containing about 200 tons of dry substance) were passed through the furnace, and for every 100 tons of dry peat a *minimum* of 5 tons sulphate of ammonia was obtained, at a *maximum* cost of £5, 8s. 3d. per ton. The moist peat is delivered into hoppers, and from these by means of automatically working sliding-doors into the furnace, through which passes a blast of air, charged with aqueous vapour, at a regulated temperature. The gases contain paraffin, tars, acetic acid, and ammonia. They are passed first through a hot scrubber, described in the patent, where the tar is retained, then through a tower, fed with a hot solution of soda or milk-of-lime, where the acetic acid is absorbed in order to be afterwards utilized, and lastly through an acid tower, where they meet a stream of hot sulphuric acid. When this acid has been completely neutralized, the formed solution of sulphate of ammonia (which is the principal object of the process) is further concentrated and allowed to crystallize. The oil is drawn off from the paraffin-oil tower, when a sample solidifies on cooling. It is then subjected to distillation to remove the lighter oils, and a crude paraffin-wax, worth £4 per ton, remains without further purification. The acetate solution from the alkali tower is evaporated to dryness and distilled with sulphuric or hydrochloric acid, to obtain concentrated acetic acid, or is subjected to destructive distillation to obtain acetone. The ashes contain potassium salts and phosphates, and can be used for manurial purposes. The [unnamed] reporter considers the Woltereck process, which is worked by the Sulphate of Ammonia Co., Ltd., to be the most economical process yet discovered for the manufacture of nitrogenous plant-food, and a great benefit to the inhabitants of the extensive tracts of land occupied by peat bogs, of which there are more than 2,800,000 acres in Ireland. Enormous peat moors also exist in the United States, Canada, Newfoundland, Sweden, Norway, Russia, and Germany (in Prussia about 5,000,000 acres, in Baden 75,000 acres, in Bavaria 150,000 acres) hitherto almost entirely useless (cf. *supra*, p. 1168).

A very favourable report on the Woltereck process has been made by the United States Consul at Birmingham (*Chem. Trade J.*, 1908, xliii., p. 224).

In a paper sent to the French Academy and read on 21st December 1908 (*Comptes rend.*, 1908, i., p. 124), Woltereck reports that he has found the nitrogen to accumulate in the residue to such an extent that it greatly exceeds the percentage of nitrogen in the peat employed. This was observed after four hours' working, but after six hours the percentage of nitrogen again diminished, ultimately down to half of the original quantity (*Comptes rend.*, cxlvii., p. 1402; *Chem. Centr.*, 1909, p. 426).

Frank and Caro, in the discussion quoted *supra*, p. 1069, altogether deny the accuracy of the statements made by Woltereck on the results of his process, more particularly his assertion that he had obtained NH_3 from atmospheric nitrogen, in addition to that produced from the nitrogen of peat itself, and they point out that the caloric energy of the peat is very incompletely utilized in the Woltereck process, which not merely furnishes no excess of heating-gas, but requires more fuel than that afforded by the peat treated.

L. C. Wolff (*Technische Rundschau*, 1909, p. 212) also criticizes the Woltereck process unfavourably. He points out that it is supposed to yield 5 parts of ammonium sulphate per 100 peat; but since the various descriptions of peat contain between 1 and 2 per cent. of nitrogen (calculated on the dry state), this would alone amount to 4·7 to 8·4 per cent. ammonium sulphate. A very great drawback of that process is the enormous waste of fuel. The circumstance that by Woltereck's process peat with 75 per cent. moisture can be worked whilst that of Frank and Caro allows only 50 per cent., is not of great importance.

Woltereck (*eodem loco*, p. 272) defends his process against the criticism of Wolff, but nothing new has come out of this controversy, and only a prolonged period of working on the manufacturing scale can lead to an ultimate judgment in this affair.

Ireland and Sugden (Ger. Ps. 175401 and 180141) pass air and steam over heated peat (or coke, lignite, coal; etc.), at temperatures not above 500° C. In this case the carbon burns slowly, without visible glow, and hydrogen is formed, which in the nascent state combines with the nitrogen of the air. Since the heat of reaction is sufficient to maintain the process without heating from without, their Ger. P. 176616 states that, after the reaction has set in, a mixture of air and finely divided water is to be introduced at the ordinary temperature. According to their Ger. P. 180141, coke, charcoal, lignite, wood, etc; may be used in lieu of peat. The optimum temperature is 400°, but temperatures between 300° and 500° C. give commercially utilizable results. Besides ammonia, also tar, hydrocarbons, and acetic acid are formed, and may be utilized.

In a further German patent, No. 205006, Ireland and Sugden prescribe dehydrating the peat mechanically down to 65 to 70 per cent. water, and passing the mixture of atmospheric air and water in the shape of spray or steam over it at a temperature not exceeding 500° C. That partial dehydration of the peat is supposed to increase the yield of ammonia, and to facilitate a constant temperature in the retorts.[1]

Guillot and Brisset (Fr. P. 375792, of 1907) burn the peat in kilns, like lime-kilns, with limited access of air, so as to make the combustion slow, with or without injection of steam, and bring the gases into contact with suitable absorbents, liquid or solid, such as superphosphates, for absorption of the ammonia. In their Fr. P. 375792, they describe a special kiln for that purpose.

Müntz and Girard (B. P. 16162, of 1906) obtain nitrate of lime by impregnating peat, arranged in beds, with carbonate of lime and ammoniacal salts, so as to form a progressive nitrification and effecting the double decomposition of the nitrate of lime, obtained by the preceding treatment, with carbonate of ammonia, produced by the distillation of the peat.

Dromain (Fr. P. 392979, of 1907) constructs flues in the peat-bog itself or its immediate vicinity, in the shape of simple trenches covered with iron plates, and in these the peat is burned. The flues extend to the ammonia-recovery plant, and artificial draught may be necessary, if the distance be great; they are packed with dry peat, overlaid with wet peat.

An apparatus for obtaining ammonia from peat is described in the B. P. 1676, of 1914, of the Rigby and Wet-Carbonizing Co., Ltd.

Jones and Suarez (Ger. P. 220670) pass air and steam over heated peat at temperatures below 500°; the gases coming out of the apparatus, which after the removal of tar, ammonia, acetic acid, etc., consist essentially of CO_2, N, and steam, are taken back into the furnace containing peat, and enter it below the zone of reaction, where they are mixed with the necessary quantity of air. This is supposed to cause a considerable saving of steam, and to allow of an easier regulation of the temperature of the reaction space.

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[1] The contention of Frank, Caro, and Wolff (*vide supra*) that there is no conversion of free atmospheric nitrogen, but only that of the organic nitrogen into peat, is also applied to the processes of Ireland and Sugden.

The process of Ward and Stanley (mentioned by Kéler, *Z. angew. Chem.*, 1909, p. 1445) does not seem to differ essentially from that of Woltereck.

Ekenberg (*J. Soc. Chem. Ind.*, 1909, p. 511) states that by the process of "moist combustion" 79 per cent. of the nitrogen contained in peat can be changed into ammonia.

Lymn (B. P. 17074, of 1909) finds that by superheating the air-steam blast before entering the producer, peat containing 60 to 70 per cent. water can be used, and that much ammonia and good gas is thus obtained. The superheating by itself is not new, but the way in which the inventor carries it out, viz., burning about 20 per cent. of the gas produced from peat of 60 per cent., and thereby overheating the air blast to be employed as above. Cf. *infra*, the detailed description of the Lymn process.

Guardabassi and Goulliard (Fr. P. 464591; *J. Soc. Chem. Ind.*, 1914, p. 473) describe a regenerative oven for carbonizing peat, etc., with recovery of by-products.

Process of Frank and Caro.—Another way of utilizing the vast stores of peat in various countries is before us in the application of the Mond gas-process, described *infra.* Peat by itself is not a very good object for destructive distillation, and A. Frank, in *Z. angew. Chem.*, 1898, p. 17, expressed himself very sceptically as to the fate of all processes for obtaining ammonia, etc., by the distillation of peat. But just the same distinguished practical chemist has later on pointed out that peat, when having been lying long enough in heaps, might be gasified, in order to supply power for central electric stations. This proposal has become much nearer to fulfilment by the observation made by N. Caro and the English Mond Company, that peat can be easily treated in Mond producers even when containing up to 50 per cent. water, and that in doing so 70 to 80 per cent. of the nitrogen contained in the peat can be obtained in the form of sulphate of ammonia, together with a very pure and uniform gas, eminently adapted for driving gas-motors. Bavarian peat, for instance, contains about 0·5 per cent., sometimes, however, up to 3 per cent., nitrogen. The latter would pay, for the Mond treatment by the ammonia alone, leaving the gas and the power obtainable by it free of expense.

The publications by Dr Nikodem Caro on that subject are found in *Z. angew. Chem.*, 1906, p. 1569; *Gluckauf*, 1907, p. 879; *Mitt. d. Ver. z. Förder. d. Moorkultur*, 1907, p. 295; *Torflager als Kraftquellen*, Danzig, 1907; *Die Stickstofffrage in Deutschland*, Berlin, 1908. The Ger. P. of Caro is 198295, the U.S. P. 970883.

A. Frank in *Z. angew. Chem.*, 1908, p. 1597, reports on the results obtained with the Mond-Caro process in working-up raw peat, with 40 or 50 per cent. water, at Sodingen, in Westphalia. This peat contains on the average 1·05 per cent. nitrogen and 3 per cent. ashes. When working-up 45 tons per day, they obtained per 1000 kg. dry peat up to 2800 cbm. gas, containing 17·4 to 18·8 vol. per cent. of CO_2, 9·4 to 11 of CO, 22·4 to 25·6 of H_2, 2·4 to 3·6 of CH_4, and 42·6 to 46·6 of N; calorific power 1400 calories per cubic metre, equal to a yield of 1000 actual h.p. hours per ton of dry peat. The yield of ammonia was up to 40 kg. sulphate per ton, *i.e.*, nearly four times as much NH_3 as the yield from real coal at gas-works and coke-ovens. When using peat, with 1 or 1·1 per cent. nitrogen at a price of 2 mark per ton in the damp state (50 per cent. water), with good wages and 15 per cent. for interest and amortization, a plant of 1000 h.p. supplies the h.p. per year at 40 to 50 mark, equal to the cheapest water-power in Scandinavia or Switzerland. In the case of "green-land" moors, with 1·5 to 2·0 per cent. N, the NH_3 pays all expenses and the power costs nothing. In this way the German moors, which cover 2½ million hectares (say 5 million acres), could be made to yield power to the amount of 3 million h.p.

The method worked out by Nic. Caro and Ad. Frank avoids the drawbacks inherent to the former processes for obtaining useful products from peat. It consists in exposing the peat in gas-producers to the action of air and steam, in such a way that the total organic substance is converted into a heating-gas, with recovery of valuable by-products. The process can be conducted in such a way that the periods of drying and of distillation are going on in the same place and at the same time, and that peat containing up to 60 per cent. water, and in the state of coarse powder, can be employed, since it anyhow arrives at the proper zone of gas-producing in the state of lump-coke. Peat of that description is obtained by spontaneous drying nearly all the year round; nor is it damaged by torrents of rain, since peat, after being dried, never takes up more than 50 to 60 per cent. water. Hence it is possible to obtain from peat *all the year round* a pure gas, possessing a strong heating power, and quite specially adapted for generating electricity, which converts the peat-bogs into sources of power of the first rank. The current generated in this way is particularly economical by the fact that, alongside with the power-gas, 85 per cent. of the nitrogen of the peat can be obtained in the shape of *ammonia*, since the "organic nitrogen" of *fresh* peat is completely transformed by steam into ammonia, whilst this is not the case with *dried* peat. The steam for this purpose is employed in excess, just as in Mond's process, and a new feature is the overheating of the mixture of air and steam to 400° to 500°, before it enters the producer. In this way from 1 ton of the peat (calculated as dry) of the ordinary contents of 1 per cent. nitrogen, roundly 40 kg. of sulphate of ammonia is obtained, together with so much power-gas of 1250 to 1350 metrical heat-units, that per ton of dry peat-substance 550 to 650, in continuous work even 900, electrical horse-power hours are obtained.

This process is, of course, only applicable on a very large scale. Its essential advantage is this: that in working up the peat only *one* by-product is obtained, which is easily saleable and stands transportation to great distances, and that it supplies power to many industries requiring a very cheap source of energy, like many electrochemical processes.

A lively controversy has arisen as to the priority of this invention, in which Lymn (*Chem. Zeit.*, 1910, p. 1355; 1911, p. 133), N. Caro (*ibid.*, 1911, p. 133), Woltereck, and others have taken part, but which we must of course leave aside here.

In the *Chem. Trade J.*, 1909, xliv., p. 81, it is claimed that the process in question is entirely a British invention, Messrs Frank and Caro being merely the consulting chemists for the German Mond Gas Company (a branch of the British Power Gas Corporation), and having published some results under their own name.

Frank and Caro energetically object to this way of stating the case. The Mond Gas Corporation (with which they are on most friendly relations) at their Staffordshire works do not gasify peat, but coal, by the "Mond gas-process," described *infra*, and they do not, like Frank and Caro, distribute electricity, but gas. The applicability of their process to partially dried peat has been proved by Caro at the Stockton works of the Mond Company, and only subsequently the Mond Company has taken up the process.

Rossi (*J. Soc. Arts*, 1915, p. 162) describes the factories at Orentano and Codigoro (Italy), where dried peat, containing 25 per cent. of water, is carbonized by the Mond process in turret-shaped ovens, 26 to 33 ft. high. From 1 ton of peat containing 2·5 per cent. N about 175 lb. of ammonium sulphate are obtained at a cost of from 4s. 10d. to 5s. 7d. per cwt. The factory at Orentano has been working since 1910, the present daily capacity being 1800 cub. ft. of peat, yielding 50 tons of ammonium sulphate per month. At the works at Codigoro, operated since 1912, 150 tons of dried peat, yielding 10 to 12 tons of ammonium sulphate, are treated daily.

F. M. Perkin (*J. Inst. Petrol. Technologists*, 1914, i., pp. 76-84) states that the destructive distillation of peat yields a thick tar containing paraffin wax, and an aqueous distillate containing ammonia, acetic acid, acetone, and methyl alcohol. The gases evolved are sufficient to carbonize the peat if it has been previously dried down to 20 per cent. water. Coke hard enough for metallurgical purposes is obtained from suitably dried briquetted peat. From 11 to 22 lb. of ammonium sulphate per ton is obtained. If the cost of dried peat does not exceed 4s. 6d. per ton, the production of oil and carbon should be remunerative.

The same author (*J. Soc. Chem. Ind.*, 1914, p. 395) discusses the recovery of by-products from peat. In England there are upwards of 6,000,000 acres of peat bog with an average depth of 12 ft. In Ireland there are 3,000,000 acres of peat bog, some of the bogs being very deep. Peat as dug contains 30 to 90 per cent. water, and must be dried down as far as 20 per cent. water, if peat coke is to be one of the by-products. Every acre would yield from 3000 to 3500 tons of such dried peat. The removal of the moisture, either by hydraulic pressure or by air-drying, is rendered difficult by the cellular structure of the peat which must be broken up by macerating-machinery, for which many patents have been taken out, or in other suitable ways. By coking Scotch peat Perkin obtained, besides oils, phenols, etc., 30·2 lb. ammonium sulphate per one ton of peat; from Doncaster peat, 21 lb. ammonium sulphate. In Canada power-gas is made from peat, for which purpose it may contain 50 per cent. moisture; the yield of ammonium sulphate is more than sufficient to pay all working expenses, so that the power-gas is obtained free of cost.

Stauber and Kochan (B. P. 41, of 1914; Fr. P. 464227) describe an apparatus for producing ammonia from peat. The Ger. P. 284178 is taken out by the Torfentgasung Stauber G. m. b. H. Inside the furnace are placed water-pipes or boxes, provided with inlets and outlets for water and steam, in such a way that they divide the space into two chambers. Steam can be passed from the top on to the red-hot mass. By means of a fireplace at the bottom of the furnace, this is brought to a red heat; when this has been attained, the fireplace is emptied and the process goes on by itself. The two chambers are worked in turns; when one of them is half finished, the other one is charged, so that both chambers are only temporarily filled. The work goes on continuously and the gas is very quickly withdrawn from the region of high temperatures, thereby producing an increased conversion of nitrogen into ammonia.

Rigby and Wet-Carbonizing Co., Ltd. (B. P. 16918, 1914; Ger. P. 275091), state that peat should be gasified by steam in such a way as to maintain a steady moisture content.

AMMONIA FROM BITUMINOUS SHALE.

The distillation of bituminous shale for the purpose of obtaining oils and paraffin is a very important industry, and has attained very large proportions, especially in Scotland, where a suitable raw material is abundant. In converting the oils, ammoniacal liquor is also obtained. According to Redwood, Bell already in 1865 made sulphate of ammonia as a by-product of treating bituminous shale in Scotland. Many of the processes latterly proposed for the recovery of ammonia from coal (see below) equally apply to bituminous shale, and need not be described here. We will mention only the patent of Playfair (B. P. 3977, 1882), who mixes with the shale, before introducing it into retorts, an alkali or alkaline earth, for the purpose of increasing the proportion of nitrogen given off as ammonia; and that of A. Neilson and J. Snodgrass (B. P. 4902, 1885), who after having worked off the whole or nearly the whole of the oil in the ordinary way, either in horizontal, or vertical, or inclined retorts, introduce a mixture of air and steam, all external heating being discontinued. The air burns the carbonaceous matter remaining in the retort, and the increased heat causes the evolution of a large amount of ammonia in addition to that obtained in the primary distillation.

In the preceding section we have noticed several processes applicable to peat and coal as well as to shale. The recovery of ammonia from shale is treated at length by Beilby (*J. Soc. Chem. Ind.*, 1897, p. 876), Redwood (*ibid.*, 1894, p. 108), Henderson (*ibid.*, 1898, p. 984), Heusler (*Berl. Ber.*, 1897, p. 2743; *Z. angew. Chem.*, 1898, p. 65), Henriques (*Chem. Rev.*, 1898, p. 61), and especially in a masterly way by Boverton Redwood ("A Practical Treatise on Mineral Oils and their By-products," London, 1897). We need not go into particulars here, as the recovery of ammonia from shale resembles very much that from coal.

The processes in which the yield of ammonia from bituminous shale is increased by means of steam, which apply just in the same manner to coal, will be dealt with in the next section.

According to Young and Beilby, Scotch shale on dry distillation yields for 100 parts of nitrogen contained in it 17.0 per cent. ammonia distilling over, 20.4 per cent. of the nitrogen being contained in the tar, 62.6 remaining in the coke. If, however, steam is blown into the red-hot retorts, as will be described in the next section in the case of coal, the proportions are changed to 74.3 per cent. as ammonia distilling over, 20.4 in the tar, 4.9 in the coke. Hence by applying 1.28 parts steam to 1 part shale, about 70 per cent. of all the nitrogen present is recovered in the shape of ammonia. The gas formed at the same time has the following composition: CO_2, 16.60 per cent.; CO, 8.10 per cent.; CH_4, 2.30 per cent.; H, 28.6 per cent.; N, 44.4 per cent.

The enormous extent which the production of ammonia from shale has acquired in Scotland will be appreciated from the statistics we shall give later on in connection with the manufacture of sulphate of ammonia. In this place we only quote the following table, found in the *Forty-third Annual Report on Alkali, etc., Works*, p. 164.

Year.	Total shale mined in the United Kingdom.	Sulphate of ammonia recovered from the shale.	Yield in lbs. per ton of shale mined.
	Tons.	Tons.	
1897	2,223,745	37,153	37·4
1898	2,137,993	37,264	39·0
1899	2,210,814	38,780	39·3
1900	2,282,221	37,267	36·6
1901	2,354,356	40,011	38·2
1902	2,107,534	36,931	39·3
1903	2,009,602	37,353	41·6
1904	2,333,062	42,486	40·8
1905	2,496,785	46,344	41·6
1906	2,546,522	48,534	42·7

1. AMMONIA FROM COAL.

Quite apart from the nitrogen forming four-fifths of our atmosphere, there is an enormous quantity of it existing in the form of organic substance and of products emanating from its decomposition. But for all practical purposes this is not of any great importance as a source of ammonia compounds in comparison with *coal*. Although only a small proportion of the nitrogen from coal is utilized in the shape of ammonia, the great bulk of our requirements of ammonia is up to the present supplied from this source.

Percentage of Nitrogen in Coal.—The quantity of nitrogen in coal is very much greater than that contained in the fresh vegetable matter which forms its original material. Such vegetable matter rarely contains more than 0·1 per cent. N, whilst in coal we find from 10 to 20 times as much. This excess of nitrogen may have been partly absorbed from the atmosphere, in the shape of ammonia, but in all probability much of it represents the remains of the animals which lived during the growth of the coal-forming forests or swamps; just as we must attribute the same origin to the nitrogenous substances contained in bituminous shales.

The amount of nitrogen in coal varies from about 1 to 2 per cent. According to Dr C. Meymott Tidy (communication to the Author), coal contains:—

From Wales	0·91 per cent. N.	
„ Lancashire	1·25	„
„ Newcastle	1·32	„
„ Scotland	1·44	„

W. Forster (*Proc. Inst. Civ. Eng.*, lxxvii., part 3, p. 23) obtained:—

From Welsh anthracite	0·91 per cent. N.	
„ English coal	1·66 to 1·75	„
„ Scotch cannel	1·28	„

Knublauch (*J. Gasbeleucht.*, 1883, p. 440) found in five Westphalian coals from 1·215 to 1·612 per cent., in two English coals 1·102 and 1·443 per cent. N.

E. Schilling ("Inaugural Dissertation," Munich, 1887) shows the most previous estimations of nitrogen in coal, made according to the method of Dumas or with soda-lime, are inaccurate, in which he agrees with Forster and Schmitz (*Stahl u. Eisen*, 1886, p. 47). By Kjeldahl's method he obtained the following results:—

Westphalian coal (Consolidation)	1·50-1·49	; average	1·50 % N.
Saar coal (Heinitz I.)	1·09-1·02	„	1·06 „
Silesian coal (Louise)	1·38-1·35	„	1·35 „
Bohemian coal (Littiz)	1·38-1·34	„	1·36 „
Saxon coal (Burgergew)	1·25-1·15	„	1·20 „
English (Bolton gas)	1·49-1·40	„	1·45 „
Pilsener cannel coal (Plattenkohle)	1·51-1·46	„	1·49 „
Bohemian lignite (Falkenau)	0·56-0·48	„	0·52 „

A great many analyses of coal, with quite similar results, has been made by Drehschmidt (*J. Gasbeleucht.*, 1904, pp. 677 *et seq.*).

Production of Ammonia in the Manufacture of Coal-gas and Coke.

Only a small proportion of the nitrogen contained in coal is utilized in the shape of ammonia. More than 90 per cent. of the coal consumed is used in such a way that the recovery of ammonia from the products of combustion is nearly or altogether impossible; and of the remaining 10 per cent., only that portion is really fully utilized for the production of ammonia from which coal-gas is manufactured; while the recovery of ammonia from coke-ovens, about which more will be said hereafter, is still comparatively little developed in most countries except Germany, but is showing a steady increase in Great Britain during the last few years, as the statistics to be given hereafter will show. A notable quantity of ammonia is also recovered at the Scottish blast-furnaces fed with raw coal (*cf.* later on).

A paper on the formation of ammonia during the carbonization of coal in an electrically heated tube has been published by Simmersbach (*J. Gas Lighting*, cxxxi., p. 246).

Since the great bulk of the ammonia compounds up to the present time is obtained as a by-product in the manufacture of ordinary coal-gas, and the latter is unlikely to increase at the same rate as the consumption of ammonia, in view of the extension of the system of electric lighting, the question must necessarily arise: What will be the state of things if the demand for ammonia should exceed the supply? That emergency seemed inevitable at one time; and in consequence of this it was at once proved that a further enormous source of ammonia was present in the method of carbonizing coal which is practised in the production of *coke for metallurgical purposes.* The progress in this direction was not at first very rapid, owing to the sudden fall in the price of ammonia, which alone proved that the demand had not as yet exceeded the supply. When such is the case, however, coke-ovens will no doubt be generally reconstructed for the recovery of ammonia as well as of coal-tar, which is always produced at the same time as the former, and of which we have treated at length in Chapter II. Only when this second source of ammonia has been drawn upon to a large extent will it become probable that the further means for increasing the production of ammonia, as described in this chapter, will be turned to profitable account.

We must, of course, refer here to the vast changes in the sources for supplying ammonia, brought about by its synthesis from elementary nitrogen, which have been discussed at length in a former part of this chapter, pp. 1054 *et seq.*

In the destructive distillation of coal, as practised at the gas-works, for the main purpose of obtaining illuminating-gas, it is necessary, in order to purify the gas, to subject it to cooling and washing with water ("scrubbing"). In this process two products are obtained from the gas—an oily and an aqueous substance, which, by settling in tanks, separate from each other, and form *tar* and *gas-liquor*. The former has been treated of at length in the preceding part of this book. The latter, which is always obtained along with tar, comes from the hydraulic main, the condensers, and scrubbers; the liquor from the hydraulic main, on account of the temperature, being poorer than that from the scrubbers. Probably in every gas-works all the liquors are united, and either sold or treated in common at the works. Some liquor always remains incorporated with the tar, and is obtained in further settling and distilling it (pp. 384 and 445); but this is comparatively a small quantity, and is generally run to waste by such of the smaller tar-distillers who have not at the same time a contract for gas-liquor.

Some more ammonia condenses in the oxide of iron purifiers, and is hence contained in the "spent oxide" (*infra*, p. 1206).

A description of the condensers and scrubbers used at gas-works, of which there is a very large variety, does not enter within the scope of this treatise, as that subject belongs to gas-making proper. (Something will be said on this head in the section on coke-ovens.) We will, however, mention that by "virgin gas-liquor" is understood that which condenses from the gas in the hydraulic main and the air condensers, and which is sometimes, but rarely, collected by itself, without mixing it with the other liquor obtained in the scrubbers, by washing the gas with water or weak liquor. Generally all the liquor runs into the same tank.

Yield of Ammonia in the Manufacture of Coal-gas.—We have seen (p. 1185) that coal contains from 1 to 2 per cent. of nitrogen. But in the process of destructive distillation nothing like the whole of this nitrogen escapes in the form of ammonia. As early as 1863, A. W. Hofmann stated that coal, in carbonizing, only yields one-third of its nitrogen, two-thirds remaining in the coke. We cannot wonder at this, if we consider that some of the well-known products of the distillation of coal-tar possessing the highest boiling-points, as carbazol and its congeners, contain 6 to 8 per cent. of nitrogen. Dr Tidy remarks that the four descriptions of coal, whose percentage of nitrogen is stated on p. 1185, if all their nitrogen reappeared in the gas-liquor, would yield per ton of coal from 142 to 226 gall. of liquor at 4° Tw.; while in practice rarely more than 45 gall. is obtained, usually only 25, in London about 13 gall.

W. Foster (*J. Chem. Soc.*, xliii., p. 105) showed that, of 100 parts of nitrogen contained in coal, there was obtained, in a laboratory experiment,

14·50 parts	as ammonia.
1·56 „	as cyanogen.
35·26 „	in the elementary condition (as part of coal-gas).
48·68 „	remaining in the coke.

Watson Smith (*J. Soc. Chem. Ind.*, 1883, p. 438) found that coal-tar, which Foster neglects in his calculations, contained 1·667 per cent. N (pitch containing 1·595, and coal-tar oils about 2 per cent.); that is, not quite 0·1 per cent. N calculated upon the coal from which the tar is derived. In coke, he found:—

Ordinary gas-retort coke . .	1·375 per cent. nitrogen.
Beehive coke	0·511 „ „
Coke from Simon-Carvès ovens .	0·384 „ „

This shows that much less nitrogen is driven out of coal during the short process of gas-making than during the long-continued processes used in the manufacture of metallurgical coke.

Cl. Winkler (*Jahresber. f. Berg- u. Huttenwesen in Sachsen*, 1884) quotes results of an experiment made in coke-ovens, where 28·7 per cent. of the nitrogen of the coal employed remained in the coke, and 71·3 per cent. escaped with the gases.

Brunet (*J. Soc. Chem. Ind.*, 1899, p. 568) was able to increase the yield of ammonia from 4·10 to 4·83 lb. per ton of coal by simply keeping a layer of water at least 3 ft. deep on the surface of the tar in the tanks.

Knublauch (*J. Gasbeleucht.*, 1883, p. 440) found, in three cases, that 31 to 36 per cent. of the nitrogen contained in the coal remained behind in the coke. Of the total nitrogen contained in five descriptions of Westphalian coal, only from 10·7 to 13·7 per cent. was recovered in the shape of ammonia;

of two English coals, 9·39 to 24·34 per cent. He estimates that of 100 parts of nitrogen there is recovered—

In the coke	31	to	36	parts.
As ammonia	10	„	14	„
As ferrocyanide in the spent oxide .	1·5	„	2	„
In the tar	1·0	„	1·3	„

leaving about 50 parts of elementary nitrogen in the coal-gas.

E. Schilling ("Inaugural Dissertation," Munich, 1887) found the percentage of nitrogen in real coal = 1·22 to 1·39, in Bohemian Plattenkohle = 1·00, in browncoal = 0·58; but with this should be combined the yield of coke, which varied from 40·5 to 74·2 per cent. of the coal; and we thus get the following table respecting the distribution of the nitrogen in coal:—

I. 100 *parts of Coal contained*

Nitrogen.	Westphalian.	English (Bolton).	Silesian.	Bohemian.	Saxon.	Saar.	Bohem. Cannel.	Bohem. Browncoal.
Total . .	1·50	1·45	1·37	1·36	1·20	1·00	1·49	0·52
Left in coke	0·96	1·02	0·95	0·77	0·86	0·85	0·56	0·23
Volatilized .	0·54	0·43	0·42	0·59	0·34	0·21	0·93	0·20

II. *Of* 100 *parts of Nitrogen reappeared*

In the coke .	80	72	70	69	64	57	44	38
Volatilized .	20	28	30	31	36	43	56	62

In order to test the actual yield of ammonia, E. Schilling made a large number of experiments at the Munich gas-works with a working retort specially fitted up for this purpose, but otherwise working under the normal conditions of gas-making and at a temperature of 1160° to 1220° C., as determined by Prinsep's alloys. He always made corresponding experiments without and with addition of lime, employing 2½ per cent. of the coal (Cooper's process).

His experiments clearly showed that the coal containing most nitrogen did not necessarily yield the highest proportion of ammonia; that even in real coal the proportion of nitrogen recovered in the shape of ammonia may vary from 6·4 to 17·4 of 100 total nitrogen, that is almost as 1 : 3; and that "liming" the coal has, in some cases, a very slight effect, and may even cause a decrease in the quantity of NH_3, whilst in other cases its effect is very considerable, viz., an increase of 30·7 per cent. in the case of English (Bolton) and of Saxon coal. It stands to reason that among the infinite variety of English gas-coals the differences will be quite as pronounced.

By a special series of experiments on a working scale, Schilling completely disproved the statement that the increase of ammonia by "liming" (cf. *infra*, p. 1200) is due to the water of hydration of the lime increasing the quantity of steam present in the retort: the contrary is decidedly the case.

Schilling believes it probable that the greater or smaller proportion of the total nitrogen has some relation to the percentage of oxygen in the coal, those coals which contain less oxygen generally giving out more of their N as NH_3 than *vice versa*. But this observation did not hold good in all cases, and would certainly require more extended investigations to be corroborated.

By experiments on the small scale, Müller (*Stahl u. Eisen*, 1888, p. 82) found that only one-fifth of the nitrogen of coal is recovered as ammonia, and that mostly during the later period of the distillation of coal. This was confirmed by Hennin (*J. Gas Lighting*, 1892, p. 296) who finds that the formation of NH_3 takes place principally about a temperature of 1000° C.; higher temperatures are not favourable, and below a bright red-heat the formation of NH_3 ceases, thus proving this to be a secondary product. The hydrogen necessary for its formation, according to this author, comes from the "constitution water" of coal, as verified by the fact that of the nitrogen of coal only 10 per cent. is transformed into NH_3 in gas-retorts or coke-ovens, but 15 per cent. in blast-furnaces with steam-blast.

The opinion formerly prevalent (*Stahl u. Eisen*, 1889, p. 482) that already at the comparatively low temperature of 780° C. a dissociation of ammonia takes place, has not been confirmed in practice; on the contrary, the formation of ammonia increases with the temperature. But according to Jicinsky (*Oesterr. Z. f. Berg u. Hütten.*, 1888, pp. 527 and 541) the nitrogen of different descriptions of coal has a different inclination to combine with nascent hydrogen. In coke-making he found three-quarters of the nitrogen to remain in the coke; of the remaining quarter, part escapes as free nitrogen or cyanogen, and only from 0·188 to 0·089 per cent. of the total N is recoverable as NH_3. This author gives a table of the percentages of a number of German and Austrian coals in nitrogen, recoverable ammonia, and tar, for which we refer to the original.

Cf. also Knublauch's later paper on nitrogen and nitrogen compounds in coal (*J. Gasbeleucht.*, 1895, pp. 753 and 769) and that of Anderson and Roberts (*J. Soc. Chem. Ind.*, 1899, p. 1099).

Drehschmidt (*J. Gasbeleucht.*, 1904, p. 682) obtained from English coal 0·176 to 0·364, from Westphalian coal 0·204 to 0·29, from Silesian coal 0·146 to 0·317 per cent. ammonia, when gasifying them at 1100° to 1200° under equal conditions.

Teodorowitsch (*Gastechniker*, xliv., part 8) quotes the yield of NH_3 obtained at the following gas-works per cent.: Cologne 0·23, Dantzic 0·25, Zürich 0·19, Dusseldorf 0·24, Basel 0·163, Nürnberg 0·139, Magdeburg 0·18. The nominal yields of ammonia obtained in different shapes are always rather higher when making sulphate than when turning it out as concentrated gas-liquor or liquor ammoniæ, because the commercial sulphate of ammonia is not quite pure, and in lieu of 25·75 per cent. contains only 23 to 24 per cent. ammonia. On the whole, we may say that good gas-coal should yield from 0·16 (as a minimum) to 0·25 parts of ammonia to 100 coal, 0·20 being a good average. But many, especially small works, get only 0·10 to at most 0·15 per cent. ammonia.

M. Mayer and V. Altmayer (*J. Gasbeleucht.*, 1907, p. 25) have investigated the influence of temperature on the formation of ammonia in the destructive distillation of coal. The different quantities of ammonia which coal yields at different temperatures depend in the first instance on the composition of the coal. Since ammonia dissociates at a high temperature, its quantity must be all the less the larger the red-hot surface and the longer the time of contact with this. The presence of carbon dioxide and monoxide promotes the liberation of the nitrogen of the coal at high temperatures, but the ammonia formed in the first instance is to a great extent split up into its elements, and this is promoted by the catalytic influence of iron or its compounds, wherefore a high percentage of ashes may be injurious to the yield of ammonia. The same coal yields less ammonia in horizontal than in vertical retorts, or in the coking process, since in horizontal retorts the gas travels above the coal along the hot surface of iron and thus the ammonia finds an opportunity for decomposing, whereas in vertical retorts it escapes in the centre through a comparatively cool kernel of coal. The maximum yield of ammonia in destructive distillation is at 800° C. At higher temperatures more nitrogen is removed as NH_3, but this is partly decomposed into its elements.

Other laboratory work on this subject has been done by Bertelsmann (*Lehrbuch der Leuchtgas-Industrie*, i., pp. 67 *et seq.*); Hilgenstock (*J. Gasbeleucht.*, 1902, p. 617); M. G. Christie ("Inaugural Dissertation," Aachen, 1906-08); Ott (*J. Gasbeleucht.*, 1909, p. 621); Bolz (*ibid.*, p. 591). Simmersbach (*Stahl u. Eisen*, xxxiv., pp. 1153 and 1209) found that the temperature of formation of ammonia varies with different coals from 800° to 900°. Decomposition of NH_3 during gasification begins at 800° and increases with rising temperature. The quantity of cyanogen formed amounts to 1·5 per cent. of the total N, and to 5 per cent. of the NH_3. Water lowers the yield of cyanogen and raises that of NH_3, while high gas velocity favours the formation of cyanogen. The size of the grain of coal has no effect on the yield of NH_3.

Very important is a report on the formation of ammonia and cyanogen during the carbonization of coal, made by Professor Simmersbach on behalf of the German Coke Oven Committee, an abstract of which appeared in the *J. Gas Lighting*, in August 1915. From his experiments the following conclusions are drawn, all of which are in accordance with former experience.

(1) The formation of ammonia occurs chiefly at a temperature where the caking of the coal has been completed.

(2) The formation of ammonia has its maximum at different temperatures for different coals.

(3) This maximum temperature varies with the nature of the nitrogen compounds in the coal, and is between 800° and 900°.

(4) The decomposition of ammonia in a concentrated gaseous state begins obviously at a temperature of 750°, and is about complete at about 800°. But owing to its dilution with other gases, the destruction of ammonia in the carbonization of coal commences at about 900°, and is increased with rising temperature.

(5) The formation of cyanogen increases with the quantity of ammonia and with the rise in temperature.

(6) The quantity of cyanogen formed in the destructive distillation of coal is about 1·2 per cent. of the total nitrogen in the coal, and about 5 per cent. of the total ammonia.

(7) Water vapour lowers the amount of cyanogen, but is favourable for the yield of ammonia.

(8) High speed of the flow of gas retards the decomposition of ammonia, and increases the formation of cyanogen.

(9) The dimensions of the pieces of coal have no influence on the formation of ammonia.

Special Processes for the Treatment of Coal-gas for Ammonia.

Claus (B. Ps. 7580, 7582, 7584, 7585, all of 1886) effects the complete purification of coal-gas by ammonia itself. He washes the gas, first by the partially saturated liquor from a former operation, afterwards by means of fresh ammonia. The liquors are heated in another apparatus to about 93, whereby CO_2 and H_2S go away with a little NH_3. The latter is absorbed in a scrubber fed with spent liquor or dilute sulphuric acid, whilst CO_2 and H_2S go into the apparatus for recovering the sulphur. The liquor, after being treated at 93°, is now heated by injection of steam, until all the ammonia, present in the free state or as carbonate or sulphide, is driven out and collected in a scrubber. The residue, containing the "fixed" ammonium salts, is employed for feeding the scrubbers, or treated in the usual way for recovering the ammonia. Of course, only a certain quantity of ammonia circulates in the system for the purpose of purifying the gas; another quantity, viz., that which is newly formed in distilling the coal, must be removed from the scrubbers in the shape of carbonate or sulphate.

Campbell and Boyd (B. P. 10186, of 1888) also employ ammoniacal liquor for purifying the coal-gas, removing at the same time the sulphur compounds by means of manganese, peroxide, suspended in the shape of mud in ammoniacal liquor, and meeting the gas in a scrubber.

Fillunger (B. P. 11077, 1906; Fr. P. 365769) uses the same liquor over and over again, after driving out the NH_3 without addition of lime.

Koppers (Ger. P. 181346; Fr. P. 356600) suddenly cools down the gases to 40° or 45° C. Thereby, together with tar, most of the ammonia, especially the combined portion of it, is precipitated along with water, and thereupon the remainder of the tar is obtained in a tar-separator. The gases are now again superheated, eventually by employing them as a cooling agent for the hot gases, so that during the absorption of the remaining ammonia in acid the latter is not diluted by the condensation of aqueous vapour. From the ammoniacal liquor first obtained the ammonia is driven out by lime and is absorbed in the same acid which has removed the remaining NH_3 from the gases.

Fürth (*J. Gasbeleucht.*, 1911, p. 1030) has put several of the new processes for treating coal-gas or coke-oven gas for ammonia in a direct way to practical tests. The introduction of the Otto process (p. 1195) at existing gas-works is not possible, but this can be done with the just-mentioned Koppers' process, by which he has obtained excellent results.

Pott (*Stahl u. Eisen*, 1912, p. 412) maintains that Otto's process is very good indeed.

J. W. Cobb (Ger. P. 275453; U.S. P. 1108705) washes the gas with an aqueous solution of zinc sulphate, to form zinc sulphide and ammonium sulphate. The latter is obtained by filtering, and evaporation; the zinc sulphide is roasted, the roasted mixture suspended in water and treated with air and sulphur oxides to regenerate the sulphate.

F. Wolf (U.S. P. 994435; Ger. P. of the Chemische Industrie Aktien-Gesellschaft und F. Wolf, 181770) passes the gas, after having removed the tar, into a scrubber, fed with water in such a way that all the H_2S remains in the gas, which is then passed under the retorts where it is burned with formation of SO_2 and sulphuric acid. On leaving the furnace, the gases go into a second scrubber, fed with ammoniacal liquor, where the sulphurous and sulphuric acid are retained; the wash gases then escape through a chimney; the liquor formed here is run into scrubbers, in counter current with air, and the ammonium sulphite is thus completely converted into sulphate.

Quite similar to this is the process described by Collett and Eckardt in Norw. P. 19972, of 1909.

Dr. C. Otto and Co. (Ger. Ps. 171203 and 174695, and appl. O8647) cool the gas in a long tube, inclining towards the hydraulic main, down to 60° to 80°. The water and tar, condensed in that tube, run in the contrary direction to that of the gas, and yield up their ammonia to it. At the vigorous cooling, which now follows, all the ammonia is obtained in the shape of a strong liquor. The ammonia obtained by running back is used in lieu of fresh water, for washing the volatile ammonia out of the gas.

Fabry (B. P. 4473, of 1910) washes the crude retort- or coke-oven gas while still warm, but after separation of the tar, by a solution of zinc sulphate. This produces a solution of ammonium sulphate which is concentrated and brought to crystallization, and a precipitate of zinc sulphide which is dried and reconverted into sulphate by roasting. This saves the sulphuric acid otherwise required for saturating the ammonia. If the H_2S contained in the crude gas does not suffice for this purpose, melted sulphur is run into the gas-retorts or coke-ovens. The sulphate produced by this "direct process" is stated to have an excellent colour and quality.

Lymn (Ger. P. 223712) describes an apparatus for recovering the ammonia from gases without towers, by means of washing-tanks.

Roelofsen (U.S. P. 960907) obtains ammonium salts, especially the sulphate, from retort- and coke-oven gases by simple apparatus, avoiding the escape of foul gases.

Heinemann (Ger. P. 138250) blows steam into the cooled crude gas, thus obtaining on condensation concentrated ammoniacal liquor and all the tar; the steam also serves for propelling the gas and dispenses from scrubbing by water.

Duvieusart (B. P. 17475, 1914; Fr. P. 475463) obtains ammonia salts by washing coal-gas with a solution of sulphites of tar-bases.

Hinselmann (Ger. P. 284641) describes his way of treating coal-gas for ammonia.

E. F. Lloyd (U.S. P. 1132594) passes the washing liquor through a cooler to a scrubber, which is supplied with fresh water, thence to a still supplied with steam, returning the exhausted liquor to the scrubber.

Theisen (B. Ps. 22433, 1910; 27696, 1911; 9618, 1914) employs centrifugal gas-washers.

Schuster and the British Coke Ovens Co., Ltd. (B. P. 6061, of 1914), purify the crude gas by passing it through a scrubber and cooler, condenser, and tar extractor, and then through an exhauster to a cooler and saturator. The ammoniacal liquor from the condenser is pumped at about 110° to an ammonia still, where it meets part of the purified gas from the pressure side of the exhauster, heated to 100° to 400°. The ammonia-laden gas then re-enters the main on the suction side of the exhauster. The gas main eventually discharges into the saturator, where the ammonia is converted into sulphate.

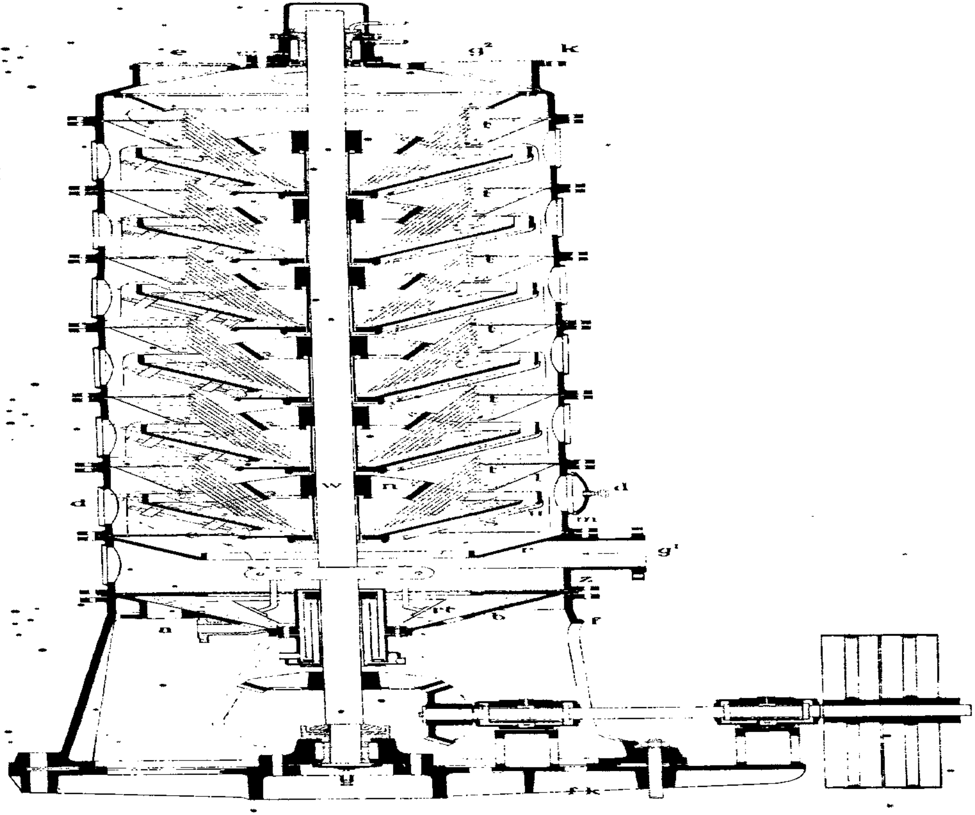
Processes of Walter Feld.—These processes bring about *the common removal of ammonia, cyanogen compounds, and hydrogen sulphide from gas* (both the ordinary coal-gas and the gases from coke-ovens), *obtaining ammonium sulphate by means of the sulphur contained in the gas.* Feld's aim was: separating the tarry matters from the gases formed in the destructive distillation of coal by chemical agents at such high temperatures that no water, or but very little of it, is taken out of the gases. This was made possible by washing the gases, first with hot tar, and then washing out the hydrogen cyanide, ammonia, and hydrogen sulphide at temperatures above the condensing-point of water—thereby avoiding both the formation of dilute ammoniacal liquor, and the conversion of HCN and H_2S into thiocyanate. He explains this in detail in *Z. angew. Chem.*, 1912, pp. 705 *et seq.* In the first instance he washes the gas with a solution of sulphate of zinc or iron, which produces the reaction:

$$FeSO_4 + 2NH_3 + H_2S = (NH_4)_2SO_4 + FeS \quad . \; . \; . \; (1)$$

The FeS is filtered off and treated with a dilute solution of SO_2, which easily and completely converts it into thiosulphate or tetrathionate:

$$2FeS + 3SO_2 = 2FeS_2O_3 + S \quad . \; . \; . \; (2)$$
$$FeS + 3SO_2 = FeSO_4O_6 \quad . \; . \; . \; . \; (3)$$

These salts act upon NH_3 and H_2S just like ferrous sulphate (equation 1), producing FeS and the respective ammonium



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To face page 1106.

salts. When the liquor, by several applications, has become concentrated, it is heated while passing through it dilute SO_2, which ultimately produces ammonium sulphate. More recently Feld has succeeded in avoiding the employment of metallic salts, by employing for washing the gas a solution, prepared from ammoniacal liquor, sulphur, and SO_2, which contains ammonium thiosulphate and polythionate. We cannot go into details on these processes, which belong to the domain of gas manufacture, but we now quote some of his patents. The last-mentioned process is called by Feld the "Polythionate Process."

Feld (B. P. 966, 1904; B. Ps. 20139 and 27567, 1907; U.S. P. 830983; Ger. Ps. 176746, 177172, 185419, 214662; Fr. Ps. 341614, 360528) separates from the gases first the tar fog in a liquid form by treating them at 100° to 200° C. with finely pulverized liquids, afterwards the aqueous vapour by cooling down to 40° C., by which process, he states, hardly any NH_3, either free or combined, is condensed. The gases, thus freed from tar and aqueous vapour, and containing nearly all the ammonia, are now absorbed in any suitable manner. In order to precipitate the tar fog in a liquid form, the hot, liquid tar itself is employed in the shape of a spray, brought into connection with the crude gases.

The same inventor, in two additions to Fr. P. 385628, prescribes avoiding an excessive lowering of the temperature by the above process, for instance, by passing the mixing gas in a counter current against the crude, hot gas. He lowers the dew-point of distillation gases of any kind by addition of vapours or steam (*J. Soc. Chem. Ind.*, 1908, p. 677). *Cf.* also his Ger. P. 208288.

Feld's Washer is shown in Fig. 237. It consists of a number of superimposed sections. Each section consists essentially of a stationary basin of smaller diameter than that of the external casing. In the centre of the latter is a vertical shaft, *w*, to which revolution is imparted by gearing at the base of the washer. To this shaft is keyed an arrangement of concentric funnels, which dip into the liquid in the stationary basins. Rotation causes the washing liquid to rise in the funnels and to be thrown as a fine spray towards the outer casing; here baffle-sheets direct the ascending gas inwards, where it is intimately mixed with the washing-liquor in a very finely divided state.

The descending liquid overflows from basin to basin. The power required for driving the apparatus, even with hot tar as the extracting fluid, is very small.

In B. P. 27568, of 1908, Feld claims the lowering of the dew-point of distillation gases by the addition of heated gases to such an extent that the temperature of the gaseous mixture remains above the desired dew-point.

The same inventor (U.S. P. 851340; B. P. 18505, 1906), in the case of gases containing less than 1 mol. CO_2 to 2 mols. NH_3, treats the gas-liquor with calcium sulphate, partly suspended and partly dissolved in water. Gases containing CO_2 may be passed in at the same time.

When employing magnesium salts for taking the ammonia out of gases which contain also CO_2, Feld (Ger. P. 185419; B. P. 26262, of 1905; U.S. P. 837045; Fr. P. 369258) adds to the washing-liquid alkaline or ammonia salts, in order to prevent a solidification of the liquid during the absorption or concentration to a stiff paste, which otherwise easily happens both in the washer and in the ammonia stills when regenerating the washing liquid. The absorbing-process is then:

$$MgCl_2 + 2NH_4Cl + 2NH_3 + CO_2 + H_2O = 4NH_4Cl + MgCO_3;$$

the boiling-off process:

$$(a)\ 2MgCO_3 + 8NH_4Cl + H_2O$$
$$= MgCO_3 . Mg(OH)_2 + 8NH_4Cl + CO_2,$$
$$(b)\ MgO . Mg(OH)_2 + 8NH_4Cl$$
$$= 2(MgCl_2 . 2NH_4Cl) + 4NH_3 + CO_2 + 2H_2O.$$

The CO_2 becoming free in (*a*) may be separately caught.

A further B. P. of Feld's is 3061, of 1909; the Fr. P. 431241 describes his "Polythionate Process."

Feld's processes are very favourably reported on in the *Forty-fourth Report of the Alkali Inspectors*, pp. 62 and 63. It is stated that his process had been very successfully employed also for the removal of dust from blast-furnace gases, up to 99 per cent. with a three-chambered washer. At a number of Continental gas-works, gas-producers, and blast-furnaces his process is now employed, also for removing lead fumes at lead-smelting works. At Mechernich an installation capable of dealing with 43 million cub. ft. of furnace-gases per twenty-four hours has been ordered.

Since 1910 Feld's process is employed at the coke-works at Monceau, at one of the New York gas-works, at the East Hull gas-works (*cf.* Rau, *Stahl u. Eisen*, 1910, p. 1241; and Lepsius, *Chem. Zeit.*, 1914, p. 747).

F. W. Wagner (*Metall. and Chem. Eng.*, 1914, p. 696) describes a plant for carrying out Feld's process.

The Process of Burkheiser.—Burkheiser, like Feld, aims at recovering the ammonia from coal-gas and coke-oven gas, together with hydrogen sulphide, in the shape of ammonium sulphate. It is described in detail by Wolfram (*J. Gasbeleucht.*, 1911, p. 325). Burkheiser's patents are Ger. Ps. 212209, 215907, 217315, 220632, 223713, 225461, 239678, 254341, 256341, 262979, 263593; B. Ps. 20920 and 21763, of 1908; 17359, of 1910; 11517 and 12227, of 1911; 8217, 15742, 15977, 16172, of 1912; 13724, of 1913; Fr. Ps. 394926, 429708, 441573, 443025, 445556, 448728, 469122; U.S. Ps. 1034974, 1073247.

Burkheiser employs the hydrogen sulphide of the gases directly for the formation of sulphate, before it leaves the apparatus. The gases mostly contain more H_2S than is required for that purpose. The gas, after removing the tar, on leaving the Pelouze apparatus is taken to a purifier, charged with a specially prepared hydrated ferric oxide, which has the composition: Fe_2O_3, H_2O, and is a far better absorbent than the ordinary purifying mass, made from bog-iron ore. This oxide is capable of purifying 20,000 times its own volume of gas, containing up to 1·5 vol. per cent. H_2S, without having to undergo a regeneration; and it is so porous that layers from 7 to 10 ft. high may be employed, and the gas may be passed through with a velocity of 150 to 200, up to 600 mm., whilst in the old processes only 5 up to at most 10 mm. are reached. Two purifiers are provided, one of which is alternately employed for absorbing H_2S, whilst the spent mass in the other purifier is regenerated by passing air through it and burning the S into SO_2. The gas coming out of the latter is passed through a scrubber, fed with a solution of ammonium sulphite, which is thereby converted into bisulphite and then serves again in the saturator for absorbing the ammonia from the gas coming out of the purifier. Hence the purifying agent always remains in the apparatus.—When the liquid is saturated with sulphite, on further supplying ammonia ammonium sulphite falls out, as this is less soluble than bisulphite. The mother liquor returns to the first saturator, where it is again saturated with SO_2. The salt is fished out and centrifugalled; it is a mixture of two-thirds sulphate and one-third sulphite, since in the recovery sulphuric acid is formed along with SO_2, and in the first scrubber sulphite is oxidized into sulphate. This mass contains 25 to 25·5 per cent. NH_3; it contains no free acid, and its manurial value, as proved by Wieler, is at least equal to that of sulphate. It can be completely transformed into sulphate by passing air through it and agitating; the sulphite is thereby sublimated, oxidized in the state of vapour to sulphate, and this is condensed in the colder parts of the apparatus.

Later on Burkheiser proposed to convert only one-third of the H_2S by his process into SO_2, and to prepare elementary sulphur by the reaction: $2H_2S+SO_2=2H_2O+3S$. Another proposal is: to pass the gas coming out of the purifier, consisting of a mixture of air, N, and SO_2, through a contact space kept at a temperature of 600°, where the SO_2 is transformed into SO_3, so that, in lieu of ammonium sulphites, sulphates are produced.

Burkheiser's process saves the expense of sulphuric acid for the manufacture of ammonium sulphate, whilst removing the H_2S and leaving a purified gas for lighting and motoric purposes; and it requires at most a third of the space occupied by the ordinary purifying apparatus of gas-works.

Processes for increasing the Yield of Ammonia in Gas-making.

1st. *By adding Alkalies or Alkaline Earths.*—The favourable influence of such an addition on the yield of ammonia may be inferred from the soda-lime method of estimating the nitrogen, practised in all laboratories for a long time past. In fact, Anderson and Roberts (*J. Soc. Chem. Ind.*, 1899, p. 1099) found that an addition of *caustic soda*, when distilling non-caking coal, liberates nearly all the nitrogen in the shape of ammonia, and when distilling caking-coal, at least increases the yield of ammonia. So also does an addition of sodium carbonate.

Lime has been recommended for this purpose already in 1875 by Knab (*Berl. Ber.*, 1875, p. 180). According to Salm, in this case the nitrogen contents of the coke is not diminished, but the yield of ammonia is increased by the splitting up of volatile tar bases. This proposal gained a temporary practical importance by the patent of W. J. Cooper (B. P. 5713, 1882). He mixes with coal, previous to its distillation, either lime, quicklime, carbonate of lime, or spent lime, the object being to obtain an increased production of ammonia, or of tar or gas. This process has been discussed by J. A. Wanklyn (*J. Soc. Chem. Ind.*, 1883, p. 438; 1884, p. 12). It is usually carried out by thoroughly mixing the slaked lime, produced from 2½ parts of quicklime, with 100 parts of coal, before charging this into the retorts. This "limed coal" is stated to yield a slightly larger fraction of its carbon in the form of volatile substances (tar and gas); also to yield a much smaller fraction of its sulphur in volatile forms, and better coke than that ordinarily obtained. In the discussion following Mr Wanklyn's papers the latter points were seriously contested. It was shown that the retention of sulphur in the coke causes a considerable loss in the value of the spent oxide, and that the quality of the coke is in reality deteriorated. But it cannot be doubted that one point urged by Mr Wanklyn is correct, namely, that by Cooper's process more nitrogen is converted into ammonia. A number of gas engineers testified to a substantial gain in ammonia; in one case it was doubled in quantity, the highest yield obtained on the large scale being about 9 lb. of ammonia (=36 lb. ammonium sulphate) per ton of coal. Whether this gain of ammonia is or is not neutralized by the expense of "liming," and the loss of sulphur in the spent oxide, is a question which must be decided by local circumstances. Only a few gas-works introduced Cooper's process; and, according to information received by the author from highly trustworthy sources in 1886, there was but little prospect of its more general adoption, as the extra yield of ammonia is counterbalanced by several drawbacks. In fact, according to the *J. Gas Lighting*, 1902, p. 1392, that process had been abandoned everywhere except at Folkestone.

From the experiments made by E. Schilling (*vide supra*, p. 1190) it appears that "liming" affects various kinds of coal very differently. Sometimes the NH_3 is slightly increased (from 3 to 11 per cent.), frequently even diminished (by 2 to 4 per cent.); a considerable increase was observed only twice out of eight cases examined, viz., 30·7 per cent. with Bolton gas-coal and

84·4 per cent. with Saxon coal. Schilling also refuted the assertion of Guéguen and Parent that the increase of NH_3 in "liming" is caused by the hydration-water of lime.

Knublauch (*J. Gasbeleucht.*, xxx., pp. 55 and 96) found that an addition of 2½ per cent. lime increased the yield of gas by 5 per cent., and decreased the quality of gas by 5 per cent. The yield of coke was slightly increased, but its heating-power on the whole remained the same. The quantity of tar was 10 per cent. less, and its quality inferior. There was an increase of 20 per cent. NH_3. The H_2S was diminished by 1·4 per 1000 coal, and in so far the purifiers had less work to do. The crude gas contained 10 per cent. CO_2 more, but most of this was removed in scrubbing.

Walton Clarke (*J. des Usines à Gaz*, xi., p. 101) found an increase of NH_3 by 39·8 per cent., and a decrease of H_2S and CO_2, with no loss in yield and illuminating-power of the gas. The coke did not suffer in illuminating-power, but its hardness falls below the allowable standard, as is explicable by the slaking of the lime on watering the coke (*Stahl u. Eisen*, 1889, p. 482).

2nd. *By Means of Hydrogen.*—R. Tervet (B. P. 1842, 1883) passes hydrogen over coal, shale, etc., in the retorts during distillation, or over the coke remaining therefrom. The hydrogen is to be obtained as in the manufacture of water-gas, or by passing coal-gas over highly heated coke. It should be used largely in excess of the quantity theoretically sufficient to combine with the nitrogen of the coke; and the same hydrogen is several times used over again in the retorts. This process is discussed at length in a paper by Tervet himself (*J. Soc. Chem. Ind.*, 1883, p. 445), from which it appears that his experiments were made only on a minute scale. He obtained ammonia corresponding at most to 83 lb. of sulphate from 1 ton of coal; but when working with "somewhat larger quantities" (2 oz. of coal!) the results fell off from 39 lb. to 67 lb.; and no experiment whatever seems to have been made on a working scale; nor is there any clue as to the probable cost of the process. We must therefore refer to the original for details.

Salm (quoted by Rau, *loc. cit.*) could not obtain any ammonia by the action of hydrogen on red-hot coke, not even by nascent hydrogen, produced from acetylene.

According to Ger. P. 153149 the gas on issuing from the retort is at once diluted with hydrogen in another retort which, it is stated, prevents the decomposition of valuable constituents, including ammonia, by the hot sides of the retort. According to Ger. P. 157740 the hydrogen is not added in another retort, but in the gasifying retort itself.

R. Maclaurin (U.S. P. 1130001) passes highly heated gas containing at least 14 per cent. hydrogen through the bed of fuel, to maintain its temperature at 700° in its lower portion, decreasing to normal temperature in the upper portion (the temperature of the lower portion in which the NH_3 is produced being maintained by enclosing it by thick refractory walls), and allowing the oils to condense on the cooler portion of the walls of the fuel chamber and of the charge, whence they are drawn off.

3rd. *By Means of Steam.*—The processes belonging to this class are hardly applicable to real illuminating-gas, and will therefore be treated separately later on (pp. 1207 *et seq.*). The proposal of Kenyon (B. P. 1016, 1886) may also be applied to ordinary gas-retorts. He erects the gas-making furnaces, which are heated from the outside, in rows two by two, so that the gases can be either taken away directly, or passed into the second furnace. The charge differs according to the products desired. For making *illuminating-gas*, one of the furnaces of each pair is charged with coal, and the gas produced therein on its way to the hydraulic main is taken through the second furnace, in order to convert the paraffinoid hydrocarbons into benzene and free hydrogen. When the charge of the first furnace has become white-hot, the connection with the second furnace is cut off, and the gas is conducted through the white-hot coke of the first furnace, whereby the free hydrogen yields ammonia. Later on superheated steam is passed in, in order to introduce hydrocarbons in one of the furnaces for being converted into benzene and free hydrogen, and to take up hydrogen sulphide in the second furnace, whereupon the operations are reversed. If *heating-gas* is to be made, nothing but superheated steam is employed, and that only in the last charged furnace, in order to prevent the decomposition of ammonia. The coke is moistened with an alkaline solution, brought to a white heat, and then superheated steam and highly heated air are passed over it. The alkaline cyanide, formed thereby, may be recovered by lixiviating the ashes; or else they are decomposed by superheated steam, in order to obtain ammonia, and the alkali recovered by lixiviation. Alkaline salts may be mixed with the coke, in order to increase the production of cyanides. The illuminating-gas receives an excess of ammonia, by being treated with ammoniacal liquor in a scrubber; the ammonium salts are then taken out of the gas by washing with water. The liquid from the washing operation is utilized by treating it in a tower with steam containing ammonia, as it goes away from the stills in which it is concentrated.

Ger. P. 153166 prescribes sending steam into the retorts where it passes through the coals and the red-hot coke; thereby less tar, but more gas (water-gas) and ammonia are formed.

C. Waldeck (Ger. P. 281096) obtains ammonia from coke-breeze by means of steam, or a mixture of steam with other gases, heating the mass by an electric-resistance apparatus.

Markgraf (*Stahl u. Eisen*, 1915, p. 905) and Sachs (*ibid.*, p. 801) discuss the influence of steam on the production of ammonia in gasifying coal. The patents of Sachs are B. P. 28755, 1913, and Ger. P. 274011.

Ammonia recovered from Coal-gas directly, without Scrubbers.

F. J. Bolton and J. A. Wanklyn (Ger. P. 16788) pass the crude gas, freed from tar, but not scrubbed, through a purifier in which superphosphate is spread out on trays; thus an ammoniacal manure is formed without having to collect and distil gas-liquor, and without wasting sulphuric acid. This process is extended by a further patent (B. P. 2709, 1882) to the gases from coke-ovens and blast-furnaces. These are passed through pipes into which superheated steam is injected, in order to remove the tar. In these pipes, plates of wire-netting or corrugated sheet-iron are placed longitudinally, to catch tar and soot. The gases are then passed through perforated trays, containing superphosphate, gypsum, or coke moistened with sulphuric acid, to condense the ammonia; if rich in ammonia, they are first passed over shallow pans filled with sulphuric acid.

Practical experiments made with this process have been described by Bunte (*Dingl. polyt. J.*, ccxlv., p. 40). The superphosphate employed was made from Mezillones phosphates, and was first neutralized by gas-liquor to prevent any free sulphuric acid from absorbing the heavy hydrocarbons of the gas. The gas was passed over this, after coming from the scrubbers, with 60 g. of NH_3 per 100 cbm.; after passing through the superphosphate the ammonia decreased to 3·4 g. In a second experiment, the scrubbed gas contained 60 g. NH_3; when scrubbing was discontinued, 108 g. per 100 cbm.; the gas issuing from the superphosphate apparatus contained at first 8 or 9, later on 12 g.; with increasing saturation of the superphosphate, at least 50 g. NH_3. If this process were to be introduced on a large scale, it would evidently be necessary to provide a series of purifiers, worked methodically, like oxide-of-iron purifiers, so that the gas should always pass in the end through fresh superphosphate.

Vorster and Gruneberg (Ger. P. 21837) pass coal-gas over trays charged with a mixture of infusorial earth (*Kieselguhr*) of flue-dust and sulphuric acid, in order to retain ammonia. Another patent (Ger. P. 25466) claims the use of a large number of other porous materials for the same purpose.

A. P. Price (B. P. 6983, 1884) claims the use of sulphuric and sulphurous acid, and of potassium, sodium, or ammonia phosphate for retaining the ammonia present in coal-gas.

Cuyper (Ger. P. 70791) absorbs the ammonia from gas by means of damp peat, which retains also the H_2S, and yields the free ammonia by heating to 40°, or at most 80° C. The residue may be used as manure.

Boerner (Ger. P. 124513) absorbs the ammonia from coal-gas by means of finely ground primeval rock, which has been treated with concentrated sulphuric acid at a temperature of 280° to 300°.

Kohlrepp and Wohl (Ger. P. 134775) employ peat or other fibrous material, soaked with sulphuric acid. The mass, when saturated with NH_3, may be extracted with water, or employed as a fertilizer as it is.

Püning (Ger. P. 245235) removes the tar fog from coal-gas, before entering into the acid bath, by electric currents of high tension, keeping the temperature so high above the dew-point that no water is condensed in the liquid form, and that a sufficient excess of heat from the superheated gas gets into the acid bath to effect a complete saturation without applying any other heating. According to his experiments the removal of the tar fog is possible at 100° and upwards, while the dew-point of normal coke-oven gas is at about 75°. The power required for this treatment is only 2 h.p. for a set of 60 retorts, which in the processes used now take 30 to 60 h.p.; and the expense of steam and lime for working up the ammoniacal liquor is saved.

The "direct sulphate process," as well as some others, is treated later on in connection with the recovery of ammonia from coke-oven gases.

Ammonia from the Spent Oxide and other By-products of Gas-works.

Part of the ammonia given off in treating coal in gas retorts remains at the purification of the gas from hydrogen sulphide and cyanogen compounds in the purifying mass (Laming, Lux, etc.), and is found in the "spent oxide," principally in the shape of ammonium sulphocyanide and sulphate, together with free sulphur and Prussian blue. These masses contain 16 to 30 per cent. water, 25 to 30 per cent. sulphur, 2 to 10 per cent. Prussian blue, 2½ to 8 per cent. ammonium sulphocyanide, 1 to 3 per cent. ammonia.

These masses are worked for the recovery of cyanogen compounds by lixiviation in sets of tanks, holding 4 to 5 cbm. The last liquors obtained thereby contain principally ammonium sulphate and sulphocyanide, in more or less concentrated form. They are worked for ammonia by passing them, together with the required quantity of milk of lime, through a column, like those to be described *infra* for the working up of gas liquor. The liquor coming out of the column is filtered, and sulphocyanide and ferrocyanide salts are prepared from it by well-known methods. Th. Richters (Ger. P. 15206) washes or steams the spent oxide every time before it is regenerated, preferably by treating it with air in a box fitted with divisions. In this way the regeneration is combined with the recovery of ammonia, since the process of oxidizing the ferrous sulphide to oxide and free sulphur evolves so much heat that the ammonia is driven off, and can be washed out of the escaping air by means of acid.

At many gas-works "cyanogen mud" is obtained in the wet gas-purifying process of Bueb (Ger. Ps. 112459, etc.). By this the cyanogen is absorbed in a cold-saturated solution of ferrous sulphate, which primarily takes up the ammonia and the hydrogen sulphide of the gas, with formation of FeS and ammonium sulphate, and later on absorbs the cyanhydric acid, with the assistance of the ammonia, the final product being an insoluble ferrocyanammonium compound, $(NH_4)_6.Fe[Fe(CN)_6]_2$, in the shape of mud. This "cyanogen mud" contains a quantity of cyanogen corresponding to 18 to 20 per cent. potassium ferrocyanide, and 6 to 7 per cent. ammonia, partly in the shape of sulphate and partly in that of ammonium ferrocyanide. It is usually transformed by caustic lime in closed vessels into calcium ferrocyanide, the ammonia distilling over in a very pure form, while the residue after filtration is worked for potassium ferrocyanide. The solution filtered from the "cyanogen mud," containing ammonium sulphate, is either worked for this by evaporation, or after addition of lime in free ammonia is driven off.

Koppers (B. P. 21385, of 1913) heats the spent oxide first at temperatures below those at which sulphur dioxide is formed, and separates the ammonia contained in the gases in the usual way.

Ammonia from Calcium-Carbonate Mud.—The Badische Anilin- und Sodafabrik (Ger. P. 281174) obtain from calcium carbonate mud containing ammonium sulphate that salt by means of submerged vacuum filters, similar to those used for the extraction of gold. The mud forms on the filter an evenly permeating layer which retains this property during the subsequent washing, and admits of getting the ammonium sulphate out by means of small quantities of water.

2. PRODUCTION OF AMMONIA BY GASIFYING COAL OR SHALE BY THE ACTION OF STEAM (PRODUCER-GAS, MOND GAS).

We have seen (pp. 1187 *et seq.*) that only a small portion of the nitrogen of coal is converted into ammonia in the ordinary process of gas-making, and that the greater portion remains behind in the coke. A similar thing happens in the distillation of bituminous shale, as carried out especially in Scotland. Hence have arisen a number of attempts at obtaining a much larger quantity of ammonia by special treatment. We may class among them already the processes enumerated in the last section; but while these still aimed at producing at the same time ordinary illuminating-gas as the principal product, we shall now speak of those processes which treat the coal for ammonia as a principal product, and obtain a gas not fit for lighting-, but only for heating-purposes, more or less like the well-known "water-gas." We have also seen (*supra*, p. 1179) that in the complete gasification of peat by the process of Frank and Caro, by means of steam and air, nearly the whole nitrogen contained in peat is recovered as ammonia, together with a gas, serving both for calorific and motoric purposes.

The first attempts in this direction on a really large scale seem to have been made soon after 1880 in Scotland, where the recovery of ammonia by distilling bituminous shale was already then vigorously carried out.

W. Young and G. T. Beilby (B. P. 5084, 1882) introduce coal-dross, shale, peat, etc., in a fine state of division into highly heated retorts, where these matters are consumed in an atmosphere of steam and air, with the production of a heating-gas rich in ammonia, along with undecomposed steam. This gas is cooled down to a certain extent, and the ammonia is then taken out by sulphuric acid, after which the gas is then ready to be used as fuel. G. Beilby has given a detailed description of this process.[1] Its principle is: distilling coal first in a current of steam, and burning the coke, which retains about 60 per cent. of the nitrogen, in a mixture of steam and air, the former being in such large excess as to preserve from decomposition the ammonia derived from the nitrogen of the coke. When this process is properly managed, ammonia is produced equal to from three-fifths to four-fifths of the nitrogen of the coal, that is—from three to four times as much ammonia as is produced by the most efficiently performed destructive distillation. This result, however, can only be obtained by the partial or total consumption of the carbonaceous residue, so that the process is only applicable to the production of gas, not of coke, from coal. One-half of the fixed carbon of coal is oxidized by the oxygen of steam setting free an equivalent amount of hydrogen. The gas obtained is very much richer in hydrogen than ordinary producer-gas, or even the gas from the Wilson producers, where steam is also used, and is therefore a more valuable fuel. This is proved by the following analyses:—

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[1] *J. Soc. Chem. Ind.*, 1884, p. 216; *cf.* also 1885, p. 220; and Watson Smith's Report, *ibid.*, p. 472, which is reproduced here.

	Wilson gas.	Young & Beilby gas.	The same, according to Lymn.
Carbon dioxide	7·14	15·40	16·6
Hydrogen	12·15	34·53	28·6
Carbon monoxide	19·83	10·72	8·1
Methane	3·91	4·02	2·3
Nitrogen	57·24	35·33	44·4
	100·27	100·00	100·0

This principle has been carried out by two different forms of gas-producers.

The first form is designed for supplying the heat for the distillation of shale. It consists of a vertical retort built of brick, closed by a door at the top, and provided with an exit-pipe which connects the retort with a system of mains and condensers. At its lower end the retort terminates in a closed fireplace as ashpit, with regulating doors or dampers. The dross or small coal is introduced by the top door, and, resting on the firebars, fills the retort from top to bottom. The upper part of the retort, being surrounded by flues through which fire-gases are led, is kept at a full red-heat. The coal in this part of the retort is distilled, and gives off gases and vapours, which pass away by the exit-pipe to be cooled and condensed. As the coke passes down in the retort, it is met by a current of steam, which is partly decomposed, burning the carbon, and producing ammonia and "water-gas," which pass off along with the other volatile products. When such coke as has escaped the action of the steam reaches the firebars, it is burned into carbon monoxide by a regulated admission of air. This red-hot carbon monoxide passes off by ports at the lower end of the retort, and is burned to dioxide in the flues surrounding the shale-retorts. The gases from the upper part of the retort, after having been deprived of their condensable constituents, are also returned and used in firing the retorts. By this system of firing, less fuel is used than by open furnaces, and the ammonia and tar recovered from the coal more than pay its first cost. About two hundred of these retort-producers were then (1882) in use in Scotch oil-works.

The second form is intended for the production of gas for firing steam-boilers or for metallurgical operations. The shell of the retort is built of grooved bricks as before, but it is of circular section and of much larger diameter than the just-described retorts. The top is closed by a shallow hopper of cast-iron, with two charging-doors; through the centre of this hopper a large iron pipe is led half-way down the retort. This pipe serves as exit for the gases, and ends at the top in a large dust-box which runs along the bench. From the dust-box the gas is conveyed by large pipes to the condensers and exhauster. The bottom of the brick retorts rests on an iron snout-piece, which is provided with a door at the outside of the brick-work. The steam and air are blown in at the front of this snout-piece. The gas and air for heating the setting rise upwards by pipes between the walls of the building, and are thereby heated before they take fire. The fire-gases surrounding the retorts are drawn downwards by chimney draught, and before entering the main flues at the bottom of the setting they give up their heat to the iron snout-pieces, through which the steam and air are entering.

Gas Condensers and Scrubbers.—In carrying out the process of gasifying carbonaceous residues by the assistance of steam, a great deal of heat is carried away from the operation by the large quantity of gas produced. To recover a part of this heat, and to make it again available in the process, certain forms of regenerative condensers have been devised. In these, the hot gases from the retorts pass through tubes which are immersed in water, or are kept wet by a shower or spray of water. The tubes are enclosed in a box or case through which a current of air is forced. The air becomes saturated with water-vapour to an extent depending on its own temperature and that of the wetted tube-surface. This air, by the further addition of steam, becomes fit for the incineration of the coal in retort gas-producers. Since the principal consumption of heat in the vaporization of water is that portion which is latent in the steam, the economy of this method of producing water-vapour by heat of comparatively low grade is very evident. Air at 65° C. takes up one-fourth of its weight of water, at 74° one-third, at 80° one-half, at 85° its own weight, and at 93° twice its weight; it is therefore possible to evaporate large quantities of water by means of a comparatively small volume of air. Condensers of this construction had in 1885 been working satisfactorily in the Clippens Company's works at Pentland for nearly two years.

Beilby states that of 100 parts of the nitrogen contained in bituminous shale (amounting to about 1 per cent.) there is recovered in distilling it in the formerly usual manner for the production of paraffin oils: 17·0 as ammonia in the watery distillate, 20·4 as alkaloid-containing tar, 62·6 in the residual coke. But if the distillation was carried on first at a low red-heat, and the residue was afterwards subjected to a bright red-heat in the presence of steam, only 4·9 per cent. of the total nitrogen was left in the coke, 74·3 per cent. being recovered as ammonia, and 20·8 as alkaloidal tar. A certain proportion of air may be mixed with the steam without seriously reducing the yield of ammonia. This has the advantage that a certain amount of heat is generated within the retort, and less heat has to be supplied from the outside.

Ingenious as the system of Young and Beilby is, we can hardly expect it to make much way at the present prices of ammonia. It must also be considered that the conditions for producing a maximum of ammonia, and those for turning out the best possible water-gas, are opposed to each other. For the former, the temperature ought to be kept down, if possible, below 500°, since ammonia, under favourable circumstances, begins to be decomposed rather below 500°, and is fully split up at 780°. But in order to realise as nearly as possible the theoretical reaction of forming water-gas,

$$C + H_2O = CO + H_2,$$

the temperature ought to be at least 900° C.; below this the reaction

$$C + 2H_2O = CO_2 + H_4$$

gets the upper hand. In fact, the best temperature for the formation of good water-gas is about 1000°.

This difficulty can be overcome on the small scale by employing an excess of steam. H. Grouven, in his analytical process for estimating the percentage of nitrogen in organic substances, passes through the apparatus a quantity of steam equal to 20 or 30 times the weight of the substance. W. Foster (see below) used 16 times the theoretical quantity. This is evidently impossible to apply on an industrial scale; but Young and Beilby have found that by mixing steam and air, 60 or 70 per cent. of the nitrogen can be obtained on the large scale as ammonia, with an expenditure of only 1¼ parts of steam to 1 part of coal. That, however, the heating-gas obtained by their mode of operation is of a somewhat poor description, can be seen from the analyses quoted above.

It must not be forgotten (and Beilby, in the above-quoted communication, fully acknowledges this fact) that, as early as 1878, Grouven (*cf.* p. 1169) had recognized that the introduction of superheated steam in carbonizing organic substances greatly increases the quantity of ammonia obtainable therefrom. Long after him, and also some time after Young and Beilby (whose patents date from 1881 and 1882), W. Foster (*Proc. Inst. Civ. Eng.*, 1883-4, lxxvii., p. 3) drew attention to the same fact. By using an enormous excess of steam (16 times the theoretical quantity) he was able to convert 61·6 per cent. of the nitrogen of coke into ammonia, 35 per cent. remaining behind, and 3·4 per cent. being unaccounted for. He assumes (but without any data to warrant this assumption) that on the large scale the amount of steam required would be "not unduly in excess of the theory." His calculations concerning the thermal value of water-gas are quite incorrect (cf. *ibid.*, pp. 65 and 76).

Hennin (*J. Gas Lighting*, 1892, p. 296), who also blows an exactly regulated quantity of air and steam into red-hot coal, so as to keep the temperature constant at 1000° C., asserts that he obtained one-half or three-fifths of the nitrogen of the coal as NH_3, together with much tar and a good heating-gas, containing 38 per cent. H, 4·5 methane, etc., 20·0 CO, 10·5 CO_2, 27 N, and O. [These results are incredibly high.]

A process, very similar to Young and Beilby's, has been patented by G. R. Hislop (B. P. 5252, 1882). H. Simon and Watson Smith (B. P. 4871, 1883) have patented the injection, into gas-retorts, coke-ovens, or gas-producers, of steam, along with hydrocarbons in a liquid or gaseous state. Whilst the oxygen of the steam unites with the carbon, a portion of the hydrogen set free unites with the nitrogen of the partially decomposed coal, forming ammonia; a portion also of the hydrogen unites with the sulphur of the fuel, so that the quality of the coke is improved by this treatment. This process has only been carried out experimentally up to the present. A similar object is aimed at by the process of H. Kenyon (B. P. 1016, 1886).

A. French (B. P. 5945, 1885) claims the following invention:—Any material containing carbon, nitrogen, sulphur, and common salt, or another suitable chloride, is heated in a kiln, air and steam being injected during the heating-process. The kiln is worked continuously. The reaction said to take place is expressed by the following equation:—

$$2NaCl + H_2SO_3 + 3H_2O + 2N + C = 2NH_4Cl + Na_2SO_4 + CO_2.$$

Nearly the whole of the nitrogen is said to be obtained as ammonium chloride, a small portion of it combining "with carbon and chloride, hydrogen, carbon monoxide, or sulphurous anhydride, to form various cyanogen compounds."

Waldeck (Ger. P. 281096) prepares ammonia from the nitrogen of coke breeze by treating it at exactly regulated temperatures, produced by electric currents of various kinds, with steam, utilizing the hydrogen produced at the same time by the reaction: $C + 2H_2O = 2H_2 + CO_2$. From 88 to 99 per cent. of the nitrogen present in the coke can thus be converted into ammonia.

J. Wolf (Ger. P. 281317) prepares ammonia from a mixture of carbon monoxide, nitrogen, and water, produced for instance by leading air over incandescent coke, and afterwards mixing it with steam or atomized water. The yield can be increased by working under pressure; the temperature should be kept between 300° and 450°.

The Mond Gas-process.

This process has during recent years taken such a considerable development that it is everywhere regarded with the greatest attention.

L. Mond (B. P. 3923, 1883), like the inventors quoted just now, utilizes the fact that a low temperature and the presence of steam in gas-producers are conducive to the formation of ammonia. Hence he introduces into the furnace a limited supply of air, loaded with water-spray or steam in large quantity. The resulting gases thereby become richer in hydrogen, and have a higher heating-power, and the tarry matter is richer and larger in quantity. The temperature may also be kept low by using air partly deprived of oxygen, *e.g.*, furnace-gases. The ammonia and tar are collected by cooling and condensing; or the ammonia may be absorbed without cooling by a solution of calcium chloride or magnesium chloride, or by sulphuric acid. The principal novelty claimed is, charging the limited supply of air with so large an excess of steam or water that the temperature of combustion does not exceed a dull red-heat. In a further patent (B. P. 8973, 1885) Mond describes special means for cooling and condensing producer-gas. He passes it through a coke-scrubber, in which it is cooled to 40° by a current of water. This water, loaded with ammonia and tarry products, is afterwards cooled by another stream of water flowing in the opposite direction; it is then again passed through the scrubber and again cooled, and so on, the same water being constantly used. As the steam contained in the producer-gas is condensed by this treatment, a quantity of water equal to the condensed steam is drawn off at intervals, and from it the ammonia is recovered. To obtain the latter immediately in the form of sulphate, the producer-gas is scrubbed with very dilute (2 per cent.) sulphuric acid; the solution of ammonium sulphate thus obtained is used over again, fresh sulphuric acid being added after each absorption, to restore the original acidity. This operation is continued till a sufficiently concentrated solution of ammonium sulphate is obtained to separate the salt from it. The tar is separated in the usual manner, and the residual gases are used as fuel. This method is said to effect a saving of most or all the fuel now used for raising steam for the purpose of working gas-producers, under the patents Nos. 3821 and 3923, of 1883 (the former of these patents does not refer to the recovery of ammonia).

Mond himself later on (*J. Soc. Chem. Ind.*, 1889, p. 505) gave some interesting details concerning his process, illustrated by diagrams (see Figs. 238 and 239). The gas produced in the generators G is passed at a temperature of 450° or 500° C.

through pipe *r* into the washers W, in which water is splashed about by paddles. Part of the water is evaporated; the remainder absorbs the ammonia and is run off from time to time to recover this. The tar condensed here is also occasionally removed. The gases leave the washer at a temperature of 100°, and containing much steam, by *g*, and enter at *a* a tower, S, filled with perforated bricks, where they are deprived of the last ammonia by the solution contained in the top tank *s*. This is a solution of ammonium sulphate, of

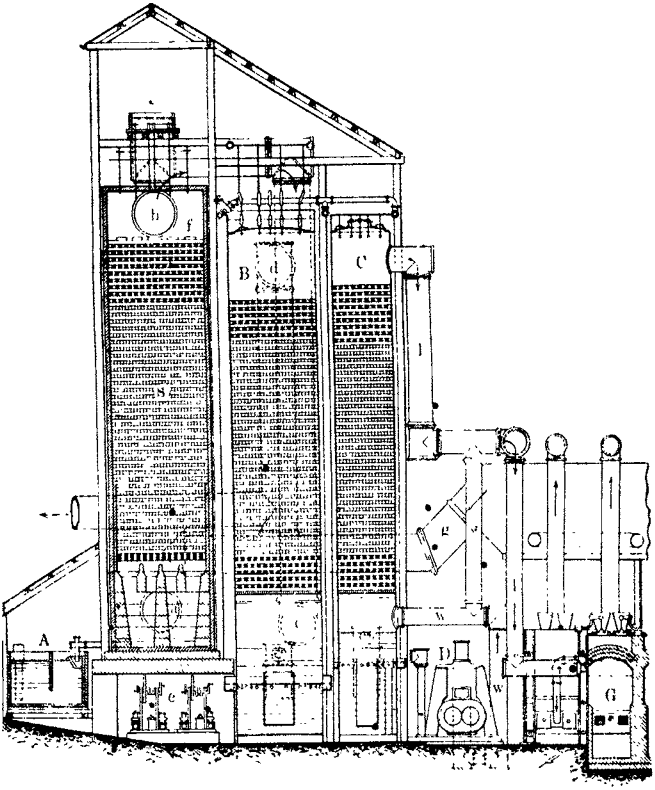

FIG. 238.

sp. gr. 1·33 to 1·36, containing 2·5 per cent. free sulphuric acid—no more, as this excess would act upon the tar and stain the liquor dark. When this issues from the tower, it passes a tar-separator, A, from which most of it is pumped back into *s* by pump *e*. Part, however, is freed from tar by treatment with heavy tar-oil, and is evaporated in leaden pans by means of a steam-coil until the mass is a thick magma. This is centrifugalled, and after washing yields good, saleable

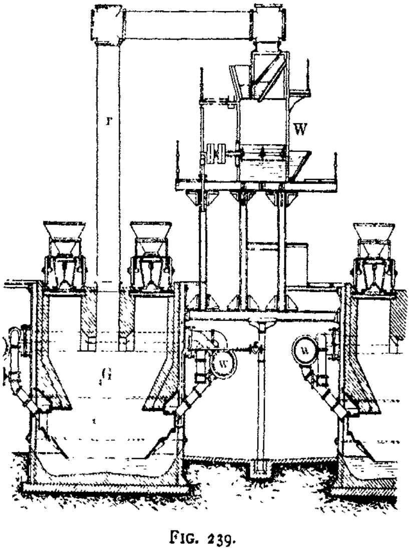

FIG. 239.

sulphate of ammonia; the mother liquor containing all the free acid is pumped back to the condensers.

When entering the tower S, the producer-gas contains 0·13 vol. per cent. NH$_3$; on leaving it, 0·013 per cent. It is at a temperature of 80° and completely saturated with steam. This is only condensed to water in the tower, B, where a stream of cold water converts the steam into water of 78°. At *d* the gas, now cooled down to 40° or 50°, leaves through *c* and is conveyed to the places where it is to be used. The hot water is first separated from tar and pumped on to a third tower, C, where it is cooled by air, forced in by the Root's blower D and pipe *w*, so that it can be again used in the scrubber B. The air is thus heated to 76° and saturated with steam, and is forced through *l* and *w* into the producer G, to which it supplies two-thirds of the steam, so that only one-third of the required quantity has to be supplied by the exhaust of the main engine.

The gas-producers G (shown on larger scale in Fig. 240) have a rectangular section (6 × 12 ft.) and are arranged in a series. The introduction of the air and the removal of the ashes take place at the shorter sides, which meet in the centre and are closed by a water-lute. The air enters under a pressure of 4 in. water; the ashes are also removed under water; but the air from pipe *w* enters above the water-level. The coal is fed in by hoppers near the exit-pipe *r*, in such a manner that the products of distillation must pass through red-hot coal, which gasifies much of the tar and keeps back the dust generated in the feeding process. The loss of coal in the ashes is only 3 or 4 per cent. of the total. The composition of the gas in the dry state is: 15 per cent. CO_2, 10 CO, 23 H, 3 hydrocarbons, 49 N. Its heating value is three-quarters of that of the coal consumed, but its utilization is much better, since it can be burned with only 2 or 3 per cent. excess of oxygen. The steam raised is 85 per cent. of what could be raised by the coal if burned on a grate. Deducting the steam introduced into the producers and required for concentrating the ammonium sulphate liquor, the above percentage decreases to 75, but is raised to 80 per cent. by the tar.

In order to recover half of the nitrogen of the coal in the shape of ammonia, 125 tons of coal must be burned in lieu of 100 tons burned in the usual way. These 125 tons of coal furnish 4 tons sulphate of ammonia, which means that for 1 ton of sulphate, 6¼ tons of coal are lost. The value of this coal at Northwich in the year 1890 was about £1, 15s.; adding the cost of extra labour, of sulphuric acid, etc., the cost of 1 ton sulphate of ammonia is from £4, 10s. to £5, that is, about half its average market price. Apart from this profit there is the advantage of very regular firing by the gaseous fuel and of avoiding all smoke.

Thus the matter stood about the year 1890, when Mond's process, apart from his own works, had been introduced at very few other places, as it cannot be profitably carried out except on a very large scale, and as the ammonia in this way is recovered at the expense of greatly reducing the caloric effect of the producer-gas, so that the process could only pay at localities where coal is very cheap.

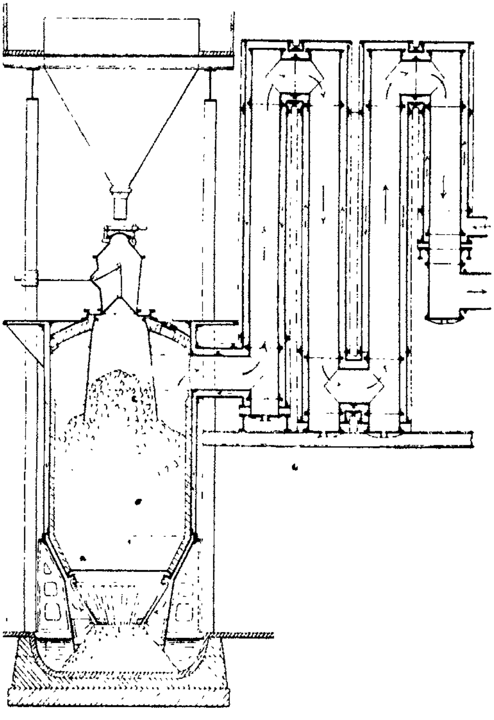

FIG. 240.

Since the plant, as constructed above, owing to the large proportion of steam in the air-blast, yielded gas below the desired standard, and less ammonia than had been expected, Mond changed the design of the gas-generating part of the plant so that the air and steam-blast enter the producer with a considerable degree of superheat, thus enabling a still greater extent to be used, as described in his B. P. 12440, of 1893, and shown in Fig. 240. The producer is of circular section, and is surrounded by a jacket through which air is passed on its way to the grate, reducing the loss from radiation and further superheating the steam and air-blast. Contiguous to the producer is arranged a superheater, consisting of a series of parallel tubes with alternate ends connected, surrounded by a series of larger tubes forming an annular space. The gas from the producer passes through the inner tubes and superheats the steam and air-blast which are passed through the annular space in a counter-current direction on its way to the producer. The gas produced was found to possess a much higher heat value, and a considerably increased yield of ammonia was obtained without extra fuel.

The Mond gas gives out only 1100 to 1200 g. calories per cubic metre, and is therefore not to be compared to coal-gas, but only to producer-gas. Its direct use under steam-boilers is not very convenient. But the introduction of gas-motors has entirely changed this. In consequence of its purity and its practically constant composition, that gas is eminently adapted for gas-motors, as proved in practice. The wear and tear of the motors, otherwise a sore point, is reduced almost to a minimum.

The Mond process and its applications to various materials are treated at length in an important paper by Nikodem Caro (*Z. angew. Chem.*, 1906, pp. 1569 *et seq.*). He sets out with a demonstration of the continuously increasing demand of nitrogenous matters for agricultural purposes, which is at present to a great extent supplied by Chilian nitrate of soda. The only important home source of nitrogen in Germany (and even more so in Great Britain!) is coal. Part of its nitrogen is already now recovered in the shape of sulphate of ammonia, of which Germany produces a considerable quantity (190,000 tons in 1905). She imported, however, in that year, still upwards of 20,000 tons of sulphate of ammonia,[1] besides 571,140 tons of nitrate of soda and 57,013 tons of guano. Her total consumption of nitrogen in all shapes in 1905 was 150,000 tons; the yearly increase of consumption of nitrogen, which formerly amounted to 6000 tons, had then risen to 15,000 tons. The solution of the question how this great and constantly increasing demand of nitrogen compounds can be met (which is, of course, equally important for Great Britain and all other industrial countries) must be looked for in two directions. One of these, the production of nitrogen compounds from atmospheric air, has been already treated by us (*supra*, pp. 1065 *et seq.*). The other is: increasing the output of ammonia in the destructive distillation of coal. No serious increase of this kind can be expected in the manufacture of coal-gas; very much more in that of metallurgical coke. In 1905, Germany produced 35,000 tons of sulphate of ammonia in gas-works (in 1906, 38,000 tons), and 168,000 tons (in 1906, 197,000 tons) from coke-ovens. Assuming that all the coke required for the manufacture of pig-iron (in 1905 it was nearly 11,000,000 tons of coke for 16,800,000 tons of pig-iron) was made with recovery of ammonia, the yearly increase in that industry (roundly half a million tons coke), with the methods in use at present, would be 7000 tons of ammonium sulphate = 1470 tons of nitrogen, against the increased demand of 15,000 tons of nitrogen for agricultural purposes, as stated *supra*. The introduction of the recovery of ammonia at all coke-works (in Germany this would yield 230,000 tons of sulphate, against 168,000 tons obtained already in 1905) would afford only temporary relief. Permanent relief must be sought elsewhere, and here Caro turns to the increased production of ammonia from coal by the Mond process. He speaks most favourably of this, and states that it has been most successful in practice. In Great Britain about a million tons of coal is worked up by that process, which yields 40 to 50 kg. ammonium sulphate per ton, against 10 to 12 kg. in the coking process. The producer-gas obtained at the same time is certainly of poor quality, 1100 to 1200 cal., but there is a large quantity of it, from 3200 to 3500 cbm. per ton of coal, and it is very suitable for evaporating purposes, and particularly, in consequence of its great purity, for the working of gas-engines. This poor gas, which cannot very well be conveyed to great distances, must be utilized on the spot, which has in many cases militated against the introduction of the Mond process, *e.g.*, in Germany. But since the spreading of electric central stations, there is a fresh chance for the Mond process for supplying the motive power for these.

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[1] In 1906, the importation of ammonium sulphate into Germany was *nil.*

In 1908, as stated by N. Caro in a pamphlet *Die Stickstofffrage in Deutschland*, p. 29, about 1,000,000 tons of coal were treated by that process, and in Germany a company had been formed to introduce it on a very large scale for motor engines. In Staffordshire a whole district is supplied by a Mond plant, consuming 400 tons of coal per day, the gas being conveyed under pressure to the various places of consumption, where it is spent in generating an electric current—thus producing not merely an economic, but also a great hygienic improvement in localities otherwise suffering under the plague of coal-smoke.

The Mond gas-process is also able to deal with the enormous heaps of poor coal-waste collecting at the pit-mouths and at the coal-washing stations. That poor coal, containing about 30 to 40 per cent. combustible matter and 60 to 70 per cent. ashes, cannot be burned on grates; it cannot even be taken back directly to the pits, in order to fill out deserted galleries, on account of its large percentage of pyrites, but it has first to weather for a year or two. But when used in the Mond process, it yields even more ammonia than corresponds to its real contents of coal, as stated by N. Caro, who obtained by that process from a ton of such "heap-coal" 25 to 30 kg. sulphate of ammonia (against 10 to 12 kg. from good coal in the coking process), and 50 to 100 h.p. hours in the shape of electric current.

From a paper by F. G. Rowan in *The Iron and Coal Trades Review*, 1908, pp. 1594 *et seq.*, we take the following statements concerning the Mond process. In the earlier practice of this process the producers were worked at "as low a temperature as was compatible with good combustion of the fuel," the air-blast and steam mixed with it being heated only to about 76° C. by means of the air-heating tower before entering the producers. In the later practice the mixture of air and steam is heated beyond that temperature, at least to 150° C., better to 250° C., by means of air-heaters which use some of the sensible heat of the gas issuing from the producers, and by means of a double casing on the producers. It was also found that the treatment of the gases by a sulphuric-acid tower (patented by Neilson in

1882, No. 440, and adopted by Mond), after bringing them into intimate contact with water, materially reduced the value of the tar, at the same time contaminating the sulphate of ammonia and imparting to it a grey colour. Rowan, therefore, holds that the most complete and satisfactory method for the removal from producer-gases of ammonia and tar in good condition, as well as sulphur vapour and vapour of water, is to cool the gases *apart from water* to atmospheric temperature and *then* to wash them with water. The tar is then easily separated from the liquors by gravity, and the NH_3 is separated as gas from the watery solution, and is then combined with uncontaminated sulphuric acid, so that pure sulphate is obtained. By these means Beilby has obtained as much as 134 lb. of ammonia per ton of coal.

The later development of the Mond gas-process is described by Heber (*J. Gasbeleucht.*, 1910, p. 421). By introducing about 1 to 1·2 kg. high-pressure steam to 1 ton of dry fuel, the gaseous mixture is improved through the formation of water-gas, and (which is the principal thing!) the gases are taken away so fast that hardly any ammonia is decomposed. The formation of tar, which is so troublesome in the case of other gasifying processes, is in the Mond processes restricted to a minimum; and the heat of the gases leaving the producer is almost entirely utilized. The regulation of the blast allows of working with nearly the theoretical quantity of air, and to recover 75 to 85 per cent. of the caloric energy, contained in the fuel, in the hot gas coming out, whilst at most 50 per cent. of that energy is recovered in other gasifying processes. A great portion of the expense of the process is covered by the ammonia obtained. For each ton of dry fuel gasified by the Mond producer there is obtained:—

Fuel.	Percentage of N.	Ammonium sulphate obtained.
English coal . .	about 1·5	40·2 to 44·7 kg.
Peat	1 to 2·3	31·2 to 93·8 „
Lignite . . .	0·7	17·8 „

that is, roundly 80 per cent. of the total nitrogen. Hence that process is of the greatest importance for the utilization of peat, on account of its high percentage of nitrogen; but it is working for peat only at the Mont Cenis pit, at Sodingen, near

Herne, and in some places in Italy. Up to 1910 the Mond process, according to Heber, had been installed as follows:—

Country.	Number of plants.	Daily combustion of fuel, tons.	Working capacity, H.P.	Provided with recovery plant for ammonia.
Great Britain	42	2249·9	221,450	11
United States	2	134·6	13,250	1
Italy	1	91·4	9,000	1
China (Hongkong)	2	68·6	6,750	...
Argentina	2	45·7	4,500	...
Japan	3	43·7	4,300	...
Egypt	1	40·6	4,000	1
India	2	39·6	3,900	...
Germany	1	20·3	2,000	1
Portugal	1	8·1	1,000	...
Bolivia	1	6·6	650	...
New South Wales	1	5·6	550	...
Altogether	59	2754·7	271,350	

The Lymn Gas-producer with Recovery of By-products.

Very important work on the production of power-gas and ammonia from fuels of all kinds has been done by Arthur H. Lymn (Sanctuary House, Westminster, London). His system is claimed to be a considerable improvement on the Mond system (for which plants have been designed and built in many places of sizes up to 10,000 to 15,000 h.p. each by Mr Lymn). The following notes are taken from Lymn's paper in the *Proc. Amer. Soc. Mech. Eng.*, 10th Nov. 1914, and from a special pamphlet issued by him. His B. P. is 8014, of 1908.

The principal new features of this system refer to the ammonia-absorption, gas-washing, gas-cooling, and air-saturating elements of the plant. These operations had been heretofore carried out in high towers packed with earthenware ring tiles, or in equally cumbersome, horizontal, luted, dasher washers. These were replaced by Lymn, first by vertical mechanical washers, in which an intensive washing of the gases was brought about by spraying the washing-liquid by means of a series of co-axial revolving discs on to collecting-cones, each of which delivered the liquid directly on to the next revolving disc below, and so on. It was found, however, that with such an arrangement the momentum of the gas was performing much more work than the mechanical movement of the discs. Accordingly, the mechanical feature of the washer was eliminated, the collecting cones were cut away to give the gas more play, and the washer now had the appearance as shown in Fig. 241. It will be seen that if plumb lines are taken down the inside edges of the collecting cones and down the outside edges of the discs, a considerable space exists between them, which is such in practice that, if no gas is passing, the water entering at the top falls straight down to the bottom. With this modified washer, a plant originally designed to deal with the gas from 45 to 50 tons of coal per day was able to deal with that from 90 to 100 tons per day, so that the capital outlay of the gas washing part of the plant was straightway reduced one-half. Such washers had been in 1914 in operation for approximately two years with entire success, and it is now possible to design washer units of this particular type to deal with quantities of gas from 10,000 up to about 1,300,000 cub. ft. per hour.

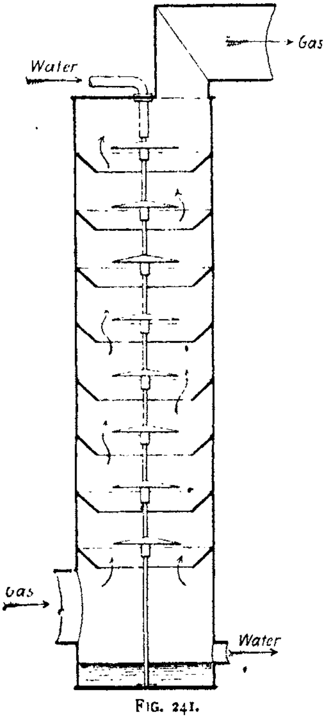


FIG. 241.

The dimensioning of the washers is not a very simple matter, being of necessity purely empirical, and the inventor arrived at the dimensions entirely by stepwise trial. An important point is that the Lymn plants do not contain any lead parts, steel being used for the parts of ammonia absorbing apparatus. A Lymn plant constructed with no lead whatever has been in operation in Germany for approximately four years, and no corrosion has yet been discovered. Its capacity is 8000 h.p.

A second direction in which Lymn claims to have made considerable improvements is in the removal of dust. These improvements have been accomplished by the adoption of a cyclonic dust separator of somewhat special design.

In the gas producer itself, Lymn has taken considerable pains to apply to ammonia recovery plants the mechanical action which has been so widely applied to ordinary gas-producers, both in the United States and in Germany, but not so much in England. This mechanical action involves agitation in the fuel and ash zones of the producer and mechanical ash removal. Many attempts in this direction of mechanical action have previously been made, and some of them have met with more or less success.

The design of producer adopted in the Lymn plants was based on the principle which has been so largely utilized for ordinary hot-gas producers in Europe, where the rotary grate and the mechanical ash removal have been further constructionally improved and very widely introduced both by Kerpely of Vienna and by Lymn's German licensees. On the basis of the last-named firm's designs as adopted for hot-gas producers, the system has been applied to ammonia recovery, material modifications being of course necessary. These modifications were to provide a vastly increased volume of air and steam, a deeper fuel bed, superheating of the blast of air and steam, increased pressure of the air blast, and consequently deeper water lutes, etc. Plants on this system have been built by the Badische Anilin- und Sodafabrik, of Ludwigshafen, and by the German Government at Heinitz. Several others are under construction. These represent the latest type of Lymn plant adopted in large-scale practice.

One point in connection with this industry deserves considerable attention. It is well known that the amount of steam generally used in these plants with normal coal is approximately 2½ tons for every ton of coal gasified. Of this amount, up to two-fifths is recovered from the heat of the gases (*i.e.*, during the gas-cooling and air-saturating cycle of operations) in a modern and properly designed plant. The remainder, 1½ tons, has, however, to be made by direct coal-fired boilers or other means. The provision of separate boilers involves a considerable charge on the operating costs of the plant, and it should therefore always be one's endeavour to obtain as large a quantity of steam as possible in the form of waste steam at practically atmospheric pressure (which is quite sufficient), or to raise such steam by utilizing waste heat.

In connection with gas-power plants, the steam can be made by utilizing the heat of the exhaust gases from the gas engines. This is a problem to which Lymn has devoted considerable attention, and in the plant referred to above, all the steam is produced in special boilers of his own design which are heated by the exhaust from the gas engines. In one particular installation there are four boilers, each attached to a 1300 h.p. gas engine, and each raising 2 to 3 lb. of steam per h.p. hour. This amount of steam is 25 per cent. more than that required for the gasification of the coal.

It might be objected that when boilers are utilized for this purpose there is danger of corrosion, but four years' full-time operation is sufficient criterion that this is not so. Lymn's experience is that satisfactory operation is merely a question of properly dimensioning the boilers.

The above-mentioned plant is absolutely self-contained as far as steam is concerned, and great strides are now being made in the Lymn plants in the matter of utilizing the heat of waste gases from all kinds of operations for the production of steam.

It may be of interest here to give some particulars of the largest gas engines, ordered from Messrs Ehrhardt and Sehmer by the Farbwerke Hoechst, Main, to be coupled to a Lymn plant consisting of five producers. The three engines are each of 4500 h.p., run at 94 r.p.m., and have only two cylinders, each of 1330 mm. (4 ft. 4½ in.) diameter and 1400 mm. (4 ft. 7 in.) stroke.

In regard to the utilization of the gas for steam-raising purposes it should be mentioned that the efficiencies which may be realized in well-constructed plants are from 70 per cent. upwards (indeed in the Bone system efficiencies of 90 per cent. or more have been actually achieved in Lymn's presence).

Considerable development in this direction of high efficiencies of gas-fired boilers is looked forward to, and Lymn has applied in most countries for patents on a different system for achieving similar results to Bone.

Lymn considers that for industries such as electrochemical plants requiring a large amount of power, it is quite unnecessary to have recourse to water powers, which (as he says) are almost invariably situated in localities quite unsuitable as manufacturing sites, and which therefore require long, costly, and unreliable transmission systems, subject to the dangers of sleet, wind, and electrical failures. Every power user who depends upon an uninterrupted supply of current for the success of his operations would gladly dispense with this transmission, even were its high cost of no importance.

In considering the development of ammonia-recovery plants, the statements made so far have referred to the treatment of ordinary *coal*, which is obviously the most used combustible. They may also be taken, however, as applying to *waste coal* containing a high percentage of ash; as well as to other poor-grade coals, such as *lignite, coke breeze, etc.*

Coke breeze, as obtained in the manufacture of lighting gas, has a particularly advantageous application in these plants. It is well known that as a general rule the retorts in gas-works are heated by means of good trade coke which has a high selling value, but the coke breeze which is sieved out is practically a waste product. This substance can now be dealt with, producing all the gas for firing the retorts together with about 60 lb. (value $1·20) of sulphate of ammonia per ton of breeze. Furthermore, much good coke is thus set free for sale to the public at a high value. A large plant is already operating on these lines in England, and is very successful and profitable.

There are, however, other combustibles whose use in producer plants is restricted on account of the high percentage of water they contain. Such in particular are *peat* and *wet browncoal.*

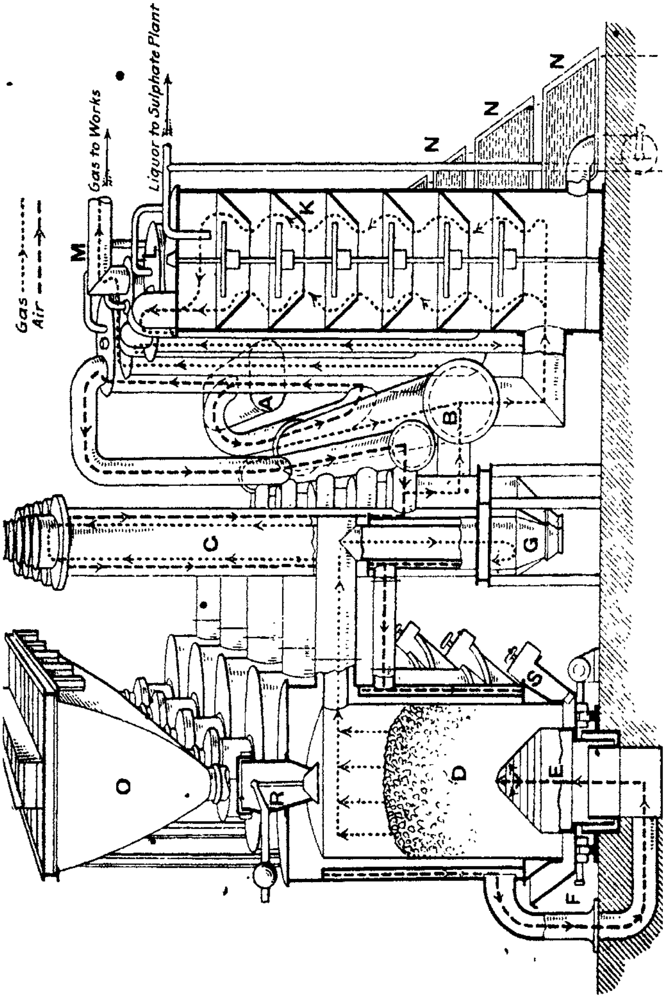
Lymn, as technical manager to The Power-Gas Corporation, was able to apply successfully his gas process to the treatment of peat between 1904 and 1907. The drying of peat is a most difficult matter, and in view of this fact it is interesting to note that to-day it is possible to produce regularly power-gas and by-products from peat containing up to 60 per cent. water. This peat can be obtained by relatively short periods of drying in the atmosphere in practically all countries. Evidences of success in this matter are the facts that a 20-ton plant was erected in Germany, some years ago, to demonstrate the advantages of this process, and another plant dealing with 100 tons of peat per day, and producing sulphate of ammonia and power-gas, has been in operation in Northern Italy for about three years. In the latter case a further peat bog has now been purchased, and a second and larger plant built upon it. Lymn has entered into a contract for building in Russia a plant of this type to treat 90 tons of peat (stated as theoretically dry) per twenty-four hours.

The quantity of ammonium sulphate produced per ton of peat depends upon the nitrogen content, and varies between 70 and 220 lb. per ton of dry peat gasified. Where peat with about 2 per cent. nitrogen is available, a large profit is obtained simply from the ammonium sulphate, regarding the gases as a by-product. Even with peat which contains little nitrogen, gas can in most cases be produced without cost.

About fifty of Lymn's producer-gas plants are already built, having a yearly fuel capacity of approximately 2,000,000 tons. These are distributed among Great Britain (which has most of them), Germany, Italy, Spain, China, Japan, and the United States. The total yearly fuel capacity of them all is close upon 2,000,000 tons. The gas from them is being used not only for power production, but also for all kinds of industrial heating operations, such as reheating furnaces, forging furnaces, annealing furnaces, steel furnaces, core stoves, crucible heating, galvanizing baths, gas-works retort firing, spelter furnaces, glass works, etc.

Fig. 242 shows the Lymn power-gas and ammonia-recovery plant.

An ordinary blower or blowers, A, are used to produce an air blast which passes through a vertical mechanical intensive air-saturating apparatus, B, in which it is brought into intimate contact with hot water (made hot by cooling the gas at a later point of the process); it thus becomes saturated with steam, and after receiving a still further supply of steam it passes into


Gas
Air
M
Gas to Works
Liquor to Sulphate Plant
K
N
N
N
L
A
B
J
C
G
O
R
D
E
S
F

the superheaters, C, in which the air and steam mixture is superheated by means of hot gases leaving the producer, D. The air and steam mixture then passes to the grate of the producer, being superheated still further on the way by passing round the producer itself.

The producer, D, which may have a mechanical or non-mechanical grate, E, according to circumstances, and the coal to be used are provided with a water seal, F, from which the ashes may be removed in the former case automatically and in the latter manually, without interfering in any way with the operation of the producers. It will thus be seen that they work day and night without cessation; indeed, practice has shown that they need not be stopped more than once in one or more years, and then only for a couple of days.

The temperature in the by-product producers is comparatively low (due to the excess steam used), which has the result that the formation of clinkers is prevented. The ammonia formed, however (despite the comparatively cool temperature of the producer), would be dissociated, were it not protected by the excess steam which is introduced for this purpose with the air blast in greater quantity than is decomposed. The hot gases containing the ammonia leave the producer at the top, pass into the superheaters, C, and superheat the air and steam blast which is passing (in the opposite direction) to the producers; at the same time the gases are cooled thereby, thus recovering a great amount of heat. On leaving the superheaters the gases, after passing through special dust-separating apparatus, G, enter the vertical intensive mechanical ammonia absorber, K, where they are brought into intimate contact with an atomized solution of sulphate of ammonia, containing small excess of sulphuric acid, which absorbs the ammonia thus produced. The said solution thereby becomes very concentrated, and requires very little evaporation for the crystallizing out of the solid salt.

From the ammonia-absorption apparatus the gases, after being freed from the ammonia, pass into the vertical mechanical intensive gas cooler, L, in which they are brought into intimate contact with cool water. The gas cooler and the air saturator work in one cycle, the water first passing through the gas cooler in order to cool the gas (the water being heated thereby), and then into the air saturator in order to saturate the air, and again cool the water ready for the gas cooler. It will be seen that by this means a very large amount of steam is recovered from the gas.

From the gas cooler, L, the gases pass to a second gas cooler, M, wherein they are brought again into contact with cold water. The gases are now sufficiently cool and clean for firing boilers or furnaces. If for use in gas engines the gases have to pass through one or perhaps two centrifugal cleaners where they are almost entirely freed from tar, from here (after traversing a special water spray separator) the gases are passed through a dry scrubber filled with sawdust or wood shavings, in which the last traces of tar are removed; the last two apparatus are not shown on the diagram. The gas is then quite clean and suitable for use in gas engines, which, indeed, can run for many months without any necessity for cleaning the valves.

The circulating vessels, designated N, receive the water or liquor from the washers, whence they are repumped to the washers.

O is the overhead fuel bunker, and R the charging hopper of the producer. S is the automatic ash-removing apparatus.

The gas produced by these plants is automatically regulated to suit all load fluctuations.

Ammonia from Other Gasifying Processes.

Pieper (B. P. 29455, 1896) obtains ammonia from coke by a continuous heating-process by means of steam in a specially constructed heating-chamber.

Aarts (B. P. 8187, 1905) describes a similar process.

Schlutius (B. Ps. 2199 and 2200, 1903) treats Dowson gas with dark electric discharges in the presence of steam and platinum sponge.

Woltereck (*Comptes rend.*, 1907, p. 929) discusses the formation of ammonia and cyanides in a Dowson gas-producer.

Clarke, Chapman, & Co. (B. P. 342A, 1907) connect the gas-producer with an apparatus for expelling the ammonia from gas-liquor, consisting of a cylindrical heat-exchanger round the producer.

Mason's Power Gas Co., Moore, Cunnington, & Stock (B. Ps. 28053 and 28054, 1908) gasify bituminous fuel, with recovery of ammonia, in a continuously working producer with three zones of different temperatures. The bottom zone, where the combustion takes place, works at 800° to 1000°, the central zone at 300° to 450°, the top zone, with a water-cooling jacket, at 80° to 150°. They blow in air and very much steam, 60 per cent. of which is decomposed (*J. Soc. Chem. Ind.*, 1910, p. 550).

Duff and the Gas Power and By-Products Co. (B. P. 4372 1910) employ the heat of the producer-gas, before it enters into the ammonia-absorbing tower, for evaporating the weak liquors, raising steam and heating up. (Former patents of E. J. Duff are 16164 and 16243, 1903.)

Aktien-Gesellschaft der Chemischen Produkten-Fabrik Pommerensdorf, and Robert Sieger (Ger. P. 281095) recover ammonia from vapours by means of acid gases, especially sulphur dioxide, in the shape of a highly concentrated solution of ammonium sulphite, and oxidizing the sulphite still left in the gas by passing it through a wooden box filled with coke or charcoal.

Several other gas-producers with ammonia recovery are described and illustrated in Lymn's above-mentioned paper.

Koppers (Ger. Ps. 257188 and 285354) prepares ammonia from carbon compounds containing nitrogen by heating in such manner that their contents of aqueous vapour is as much as possible retained.

Wahlen and Caro (B. P. 13668, 1907; Ger. P. 198295) treat the material forming the "waste, or dirt heaps" of collieries, mixed with waste coke from coke-ovens, in an externally heated shaft-furnace through which steam is passed. Combustible gases and porous coke are obtained, and the nitrogen of those materials is converted into ammonia, which may be recovered from the gas. The waste coke used with the coal prevents the material from caking in the furnace. According to a further patent of the same inventors, No. 13669, 1907, they treat the material of those "waste heaps" (which may contain twice as much nitrogen as corresponds to their contents of pure coal) in a gas-producer by the Mond process (*vide supra*, p. 1213); that is to say, with restricted supply of air and with excess of steam, in order to obtain both ammonia and power-gas. The ordinary process, where there is an excess of steam and restricted supply of air, is not available for the dirt heaps, because the materials enter into fusion in that case. The above treatment also destroys most of the pyrites, so that the material cannot spontaneously take fire, and can be employed for filling up disused adits. (The same invention forms the subject of Nikodem Caro's Ger. P. 198205.)

The Mond process can be applied also to a peculiar mass, forming at the bottom of some dried-up lakes in Germany, and called "Schlick" or "Faulschlamm," whose organic substance entirely resembles that of cannel or Boghead coal, and which contains up to 4 per cent. of nitrogen. Caro treats this matter at length in his papers. Its application to the treatment of *peat* has been referred to *supra*, pp. 1179 *et seq.*

Crosby and Rigby work on similar lines. Their B. P. 24144, of 1906, refers to a former patent, No. 20716, of 1901, according to which the water-vapour and tar are condensed before the ammonia is absorbed, by means of a washer, split up into compartments, in which the washer travels from the cooler to the hotter end, and when heated, is pumped up through an air-tower, by which means it is cooled and can be used over again in the washer, while the air is supplied with steam, and is then used in the producer. The NH_3 going away at the same time, is passed on to an absorbing-tower. According to the new patent, some sulphuric acid is added to the water, so that a fairly concentrated solution of ammonium sulphate is circulated instead of water, but always containing a certain percentage of free acid to absorb NH_3. Portions of the liquor are taken off as required for further concentration and crystallization in the usual manner.

The *Forty-fourth Annual Report of the Inspectors on Alkali, etc., Works* (for the year 1907) states that a rapid extension of producer plants with recovery of ammonia had taken place in England and Scotland during the past four years. The production of ammonia from this source has risen more than five-fold in this period, that of the United Kingdom tenfold since 1898. Most experts assume that ammonia recovery will not pay for less than 50 tons of coal a day carbonized, but recently an eminent firm of gas-engine makers has adapted it to small producers, gasifying bituminous coal for gas-engine use. It is too soon to speak with confidence as to their success in the hands of ordinary unskilled workmen.

3. AMMONIA FROM COKE-OVENS.

Since the recovery of ammonia as a by-product of coke-making is always carried on *pari passu* with that of tar, we have already described this industry in full detail in Chapter II., pp 87 *et seq.* We have also seen (pp. 162 *et seq.*) what proportions this industry has already assumed, what quantity of ammonia might be obtained from that source, and that it is just this enormous accession to our sources of ammonia (and tar) which is keeping down the prices and rendering the recovery of by-products in coke-making in many cases a process of doubtful economy. Still it can hardly be doubted that it is only a question of time when the fearful waste of useful material now going on in coke-making will be a subject of the past, and when it will appear wonderful that it was ever allowed to go on, after it had once been recognized that this need not be the case, and that good coke can be made along with tar and ammonia. Undoubtedly a certain lowering of prices may have to take place; so long as a large quantity of the tar has to be burned as fuel, in which case it may claim to be of decidedly more value than retort-coke, its price can never greatly exceed that of coke; and the price of ammonia will not merely be kept down by the over-production but also by the competition of nitrate of soda. But fortunately we are not so placed that no reasonable outlet can be found for the products in question; just as there is no limitation to burning tar as fuel, and that at the gas-works themselves, so agriculture is able to take up practically all the ammonia which industry may offer to it, if only the price is low enough. Indeed, in this seems to be the only chance of maintaining a considerably larger population out of the produce of the soil than is done at present. But of course the profits of gas companies on tar and ammonia will inevitably be greatly reduced, and compensation will have to be sought elsewhere.

In the working of coke-ovens for the recovery of by-products the mixture of gases and vapours evolved gets away from the ovens at a temperature of about 250°. The gases (about 300 cbm. per ton of coal) contain, besides tar and ammonia, the steam produced by the 10 to 15 per cent. of moisture present in the coal, and 2 to 7 per cent. produced by the carbonizing process; also more or less combustion products of the gaseous fuel, the quantity depending upon the construction and tightness of the ovens.

The object of the coke-oven industry is entirely different from that of the manufacture of illuminating-gas. The former aims at fixing as much as possible of the carbon of coal in the shape of coke; the latter, on the contrary, must tend at volatilizing the carbon to the greatest possible extent in the shape of light-giving hydrocarbons. This difference influences to begin with the choice of the coal submitted to gasification, so that "coking-coal" and "gas-coal" are kept apart; but the nitrogen percentage is practically the same in both descriptions, usually between 1 and 2 per cent. Of course the final products in both cases are the same: gas, ammoniacal liquor, tar, and coke. But the value of the two principal products, coke in one case, gas in the other case, differs immensely. According to Rau (*loc. cit.*) the value of the various products in both kinds of industries bears the following proportions to the total value realized:—

	At gas-works.	At coke-works.
Gas	75 per cent.	...
Coke	20 ,,	72 per cent.
Tar	2 ,,	5 ,,
Ammonia	3 ,,	15 ,,
Cyanogen compounds	0·3 ,,	... ,,
Benzol	... ,,	8 ,,

Therefore the economical part played by the by-products, and more especially that of ammonia, is of far greater importance at coke-works than at gas-works, and there is far more call for their complete recovery by cheap methods in the former than in the latter case. Although, therefore, at gas-works a complete purification of the gas is far more momentous than any profit made on the by-products, yet the manufacturers of coke formerly adopted the methods for separating the by-products from the gas-works, where they had attained a high degree of perfection. This state of matters has recently changed, since the manufacturers of coke have paid greater attention in the construction of the recovery plant to their particular conditions; and this has led to the invention of apparatus and processes of their own, which nowadays must be taken notice of by the gas manufacturers, who are all the more called upon to make as much as possible of their by-products, since they have now to face the competition of cheaper gaseous sources of light and power, more particularly just that of the coke-oven gas.

Direct Sulphate Processes.

We have already described in Chapter II. the processes of Brunck, Otto, Koppers, and others, which recover the ammonia, besides the tar, directly from the coke-oven gases in the form of solid sulphate. In this place we shall discuss at greater length the means by which the *direct sulphate process* can be carried out, basing on the caloric conditions.

According to Peters (*J. Gasbeleucht.*, 1908, pp. 465 and 1114) 1 cbm. dry crude coke-oven gas at 0° and 760 mm. barometric pressure contains 10·2 to 12·6 g. ammonia, and from 144 to 747 g. aqueous vapour, of which on cooling so much is precipitated in the liquid state that the gas remains saturated with moisture; *e.g.*, in the most unfavourable case (747 g. H_2O) at 0° 743 g., at 30° 712 g., at 70° 391 g., at 80° 42 g., at 81° (the dew-point), and above this nothing. The water thus precipitated contains all the "fixed" ammonia (that is on the average 10 to 15 per cent. of the total NH_3) and so much volatile ammonia that its tension in the liquor is equal to that remaining in the gas. At ordinary temperatures about one-half of the ammonia is thus taken out of the gas. On expelling the NH_3 from the gas-liquor, about 3 kg. steam go away from 100 kg. gas-liquor. If the gas, containing this aqueous vapour together with the ammonia, is passed into the sulphuric-acid bath, the formation of sulphate sets free a quantity of heat which may be taken = 40 heat units for 34 g. NH_3. The calculations made by Rau (*see* p. 1048) and the curves based thereon show that the gases may be cooled down to 5°, without having to reheat the acid-bath. Only in the case of gases containing a great deal of "fixed" ammonia, especially chloride, the gases must not be cooled down too much, but as a rule this is not necessary.

The direct sulphate process causes a very considerable saving of wages, steam, and interest on the cost of plant, and an increased recovery of ammonia, in comparison with washing this out of the gas by scrubbers, and treating the liquor thus obtained for sulphate in the ordinary way. Moreover, the trouble caused by the waste liquor of the ammonia stills, and the foul gases escaping in the saturation by sulphuric acid is altogether avoided.

Publications on this subject have been made by Rau (*loc. cit.*), Schreiber (*J. Gasbeleucht.*, 1910, p. 254), Hilgenstock (*Stahl u. Eisen*, 1909, pp. 1644 and 1687), Still (*Glückauf*, 1911, pp. 1510, 1549, 1600), Koppers (*Z. angew. Chem.*, 1911, p. 1445), Korten (*Glückauf*, 1913, p. 1102), Ohnesorge (*Z. angew. Chem.*, 1914, (pp. 378 and 525); Bagley (*Chem. Ind.*, 1914, p. 574).

The definitive result (according to Still) is that in the treatment of saturated gases the heat set free by the combination of ammonia with sulphuric acid is widely sufficient, not merely for covering all losses by cooling, etc., but for allowing to make a large addition of further liquor.

The Bergwerksgesellschaft Trier (Ger. P. 286606) describe a heating-apparatus for the direct sulphate process.

The Berlin-Anhaltische Maschinenbau A.-G. (Ger. P. appl. B74895) treat the products condensed in the direct ammonia-recovery process at higher temperatures with sulphuric acid, before they pass into the saturator, in order to convert the ammonium chloride into sulphate. The hydrochloric acid liberated thereby covers the expense of the process, and there are no troublesome waste effluents.

Recent Improvements in the Recovery of Ammonia from Coke-oven Gases.

Koppers (Ger. P. 283132) improves the yield of ammonia in coking coal by moistening the dry coal-dust before coking with a solution of soap.

The recovery of ammonia by the processes of Feld and several others, as described *supra*, pp. 1196 *et seq.*, in connection with coal-gas, is also applicable to ammonia.

Strommenger (*Glückauf*, 1915, xlix., p. 1698; 1915, li., p. 138) passes the coke-oven gases in a finely divided form through tar or an oily medium which retains most of the tar and the naphthalene.

Recovering Ammonia by Means of Sulphur Dioxide.

Of great importance are the processes for recovering the ammonia by means of *sulphur dioxide.* Some of these are of ancient date, of course applied to coal-gas, as coke-oven gases were not in question at that time. We mention the proposal of Laming (1852) for combining the NH_3, driven out of gas-liquor, with SO_2; Young (B. P. 1310, 1889); M'Dougall (B. P. 15496, 1884).

The processes of Burkheiser (*supra*, pp. 1199 *et seq.*) also belong to this class; also that of F. Wolf (*supra*, p. 1194).

The Badische Anilin- und Sodafabrik (B. Ps. 12845 and 14114, of 1912: Ger. Ps. 270379, 270574, 273306, 273315, 276490; Fr. P. 452961) heat ammonium bisulphite, preferably in aqueous solution, in the presence of a suitable catalyzer, preferably sulphur, at an initial temperature of 50° to 100°; selenium, tellurium, arsenic, or their compounds, besides many metals, oxides, and salts are also applicable. A small quantity of ammonium bisulphite solution may be first decomposed, thus producing some sulphur, and thus further quantities of solution are gradually added, so that the process is continuous. Or a solution of ammonium bisulphite, without addition of sulphur, may be subjected to local heating (*e.g.*, by pumping a concentrated solution through tubes at about 180° under 10 to 15 atmospheres' pressure); ammonium sulphate and sulphur are thus formed. The reaction may also be affected in the presence of the normal sulphite, this being mixed in a proportion somewhat less than that indicated by the equation:

$$6NH_4.H.SO_3 + 3(NH_4)_2SO_3 = 6(NH_4)_2SO_4 + 3S + 3H_2O.$$

The solution of sulphate produced is preferably saturated with ammonium bisulphite, or treated with ammonia and sulphur dioxide, when the ammonium sulphate crystallizes out and liquor for a fresh operation is obtained. The temperature is regulated, if necessary, by cooling means. Extremely small quantities of selenium are sufficient to promote this reaction, and in this case a temperature of 60° or below is sufficient. The U.S. P. 1063007 of Bosch, Mittasch, and Hecht, assigned to the Badische, describes the same process; also U.S. P. 1106919.

The Chemische Fabrik Pommerensdorf and R. Siegler (Ger. Ps. 281095 and 281174) obtain ammonia contained in gases and vapours in the shape of a concentrated solution of its salts by means of acid gases, more particularly such as contain sulphur dioxide. The ammonium sulphite is partly obtained in the condensed liquor and partly from the vapours by oxidation into sulphate.

Peacock (U.S. P. 1123584) passes a gaseous mixture, obtained by burning sulphur in a limited quantity of air, over carbon heated to 800°, to form a compound of sulphur, carbon, and nitrogen, from which ammonia is subsequently produced by treatment with hot water.

Vide also p. 1246, the process of J. and J. Addie for recovering ammonia from blast-furnace gases in the form of sulphite.

Bambach & Co. (Ger. P. 279953) absorb the NH_3 by means of SO_2 and water, and convert the ammonium sulphite thus formed into sulphate by digesting the solution with calcium or strontium sulphate, which thereby pass into sulphites. These are separated on a vacuum filter, and either sold in that state, or reconverted into sulphite by means of sodium bisulphate:

$$CaSO_4 + 2NaHSO_4 = Na_2SO_4 + H_2O + SO_2 + CaSO_4.$$

Collett and Eckardt (Ger. P. 268497) prepare by the direct union of NH_3 and SO_2 in the presence of water a solution of neutral ammonium sulphite, which is treated in another apparatus, if necessary with heating, with gas mixtures containing oxygen and at the same time with NH_3, corresponding to the progressive oxidation of the sulphite. An intermediate compound is formed which contains NH_3 and SO_2 in the proportion 1 : 2·73.

Collett (B. P. 3124, of 1913; U.S. P. 1076747; Ger. P. 283161; Canad. P. 157522) causes oxygen or a gas containing it to circulate through ammonium sulphite solution in such a way that the gas passing through the oxidation system exceeds the amount of gas supplied to or withdrawn from the system.

Condensing Apparatus for the Ammonia from Coke-oven Gases.

This apparatus, of course, resembles that used for the gases from gas retorts.

Concerning the details of condensing-apparatus, we refer to Chapter II.; also to Bolton and Wanklyn's proposal for treating the gases by superheated steam, and then passing them through commercial superphosphate in order to absorb the ammonia (p. 1204). We mention here as specially intended for the gases from coke-ovens, a patent of P. Frauencron and H. Strack (Ger. P. 32691), according to which hot coke-oven gases are passed through a mixture of coal- or coke-cinders (ashes), as they are produced in metallurgical operations, with coal-duff and lime, and thence passed into the ordinary condensers.

We shall also describe an apparatus patented by Zschokke, especially for a better condensation of ammonia. He constructs wooden shelves (Fig. 243) of flat, rounded staves, conical below, and provided with projections for the drops to fall off. The pressure in the apparatus ought to be = zero, and the gas should be very equally divided, as shown in Fig. 244. The free space is about one-third of the total surface, and it is

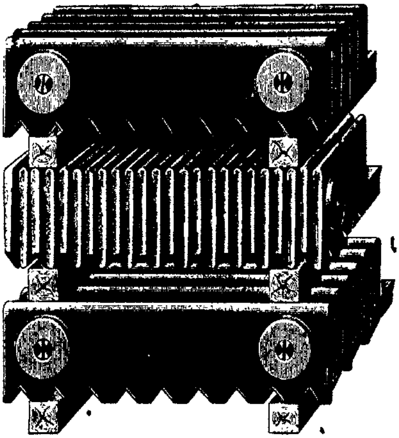


FIG. 243.

stated that the absorbing surface is 9 to 11 times greater than in the case of the ordinary perforated iron shelves. The water is supplied as shown in Fig. 245. It enters at *a* and is regulated

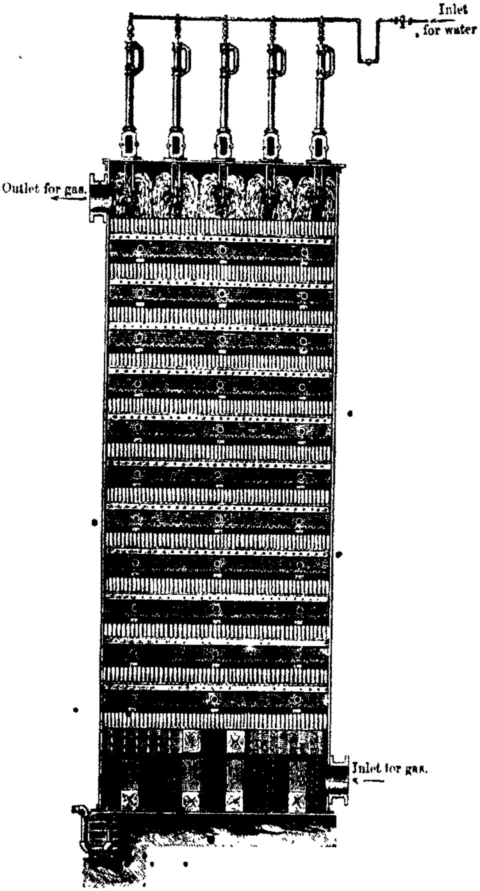


FIG. 244.

by tap *b*. The lantern *c* allows the formation of the drops to be observed. *z* is a stuffing-box; the wire *h* removes any obstruction when pushed down. The water falls 3 ft. 3 in. from the tuyere *f* down to the concave plate *d*, and is thus converted into a spray, which quite evenly wets the shelves if there is about one such tuyere for each 2 superficial feet. This admits of the supply of water being confined to less than a gallon per ·100 cbm. of gas (3500 cub. ft.), and also of obtaining very strong ammonia liquor. Plate *d* can be removed through door *e* and cleaned.

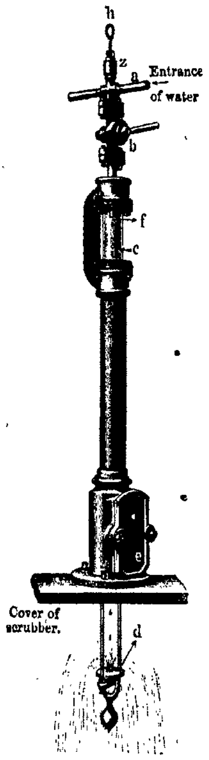


FIG. 245.

Fig. 246 shows a plant erected at the coke-works of Messrs Rud. Boecking & Co., near Brebach, and serving for 1,750,000 cub. ft. of gas in twenty-four hours. By this system only 1 g. NH_3 is left in 100 cbm. gas, against 60 or 80 g. with ordinary perforated plates (patentee's statement).

C. Otto and Co., whose coke-ovens with recovery of by-products we have treated at length on pp. 105 and 111 *et seq.*, in Ger. P. 171203, of 1906, describe an arrangement intended for a better separation of the products of condensation. By means of a reflux conduit, inclined *towards the receiver*, all products of condensation, not merely tar but also ammoniacal liquor, are conducted back to the receiver, thus producing a mixture of the hot gases coming from the receiver and the backstream of gases, which, on passing the liquids running back, cause a very good cooling and condensation of ammonia and benzol. According to their Ger. P. 174695, the ammoniacal liquor formed in running back, after cooling down, is employed for washing the gases and thus obtaining the volatile ammonia.

Brunck (B. P. 26253, of 1898) utilizes the combustion air to be fed to the ovens for the condensation of the by-products.

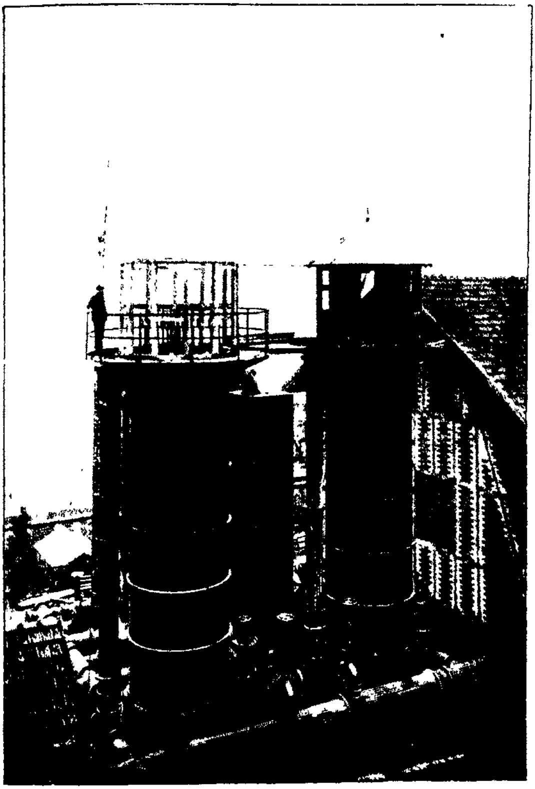


FIG. 246

[*To face page* 1242.

Heinemann (Ger. P. 166380, 1906), in order to get rid of the tar when recovering the ammonia from coke-oven gases, passes these by means of a steam injector into the bath of acid at such an angle that they blow away the tar and make it run away. Through the injector at the same time enough fresh acid is carried into gas to saturate all the NH_3. The acid tank may also be constructed with a partition over which the blown-away tar flows into a separate compartment.

Brunck (Ger. P. 167022; B. P. 23984, 1904) passes the coke-oven gases in a state of fine division through sulphuric acid of sp. gr. 1·7, at such a temperature that the ammonium salts formed separate out in a solid state and can be ladled out, fresh acid being run in as required. The required temperature is produced by the hot gases themselves.

Brunck's Ger. P. 181384 and Fr. P. 356589 prescribes taking most of the tar out by centrifugallizing the gases before they enter the absorbers.

Reininger (Ger. Ps. 166719 and 167033, 1904) adds to the coke in the ovens calcium carbide, made up into blocks by means of dehydrated tar or other non-aqueous organic agglutinating matter, and during the operation passes nitrogen or gases rich in nitrogen through the oven, in order to increase the yield of ammonia. By Ger. P. 168939 he protects the addition of a mixture of hot dehydrated tar and calcium cyanamide to the coal before coking.

Duff's Fr. P. 352180 treats the gases first in a washer, then in a tower for absorbing the NH_3, and lastly in a cooler. The liquor condensing in the latter is used again in the washer, until it is strong enough to be united with that from the absorbing-tower.

Mars, Buqua, and Laurette (Fr. P. 355375) absorb the NH_3 of the distillation gases by peat or sawdust, impregnated with sulphuric acid, and employ the product obtained directly as a fertilizer.

Andrew Short (*J. Soc. Chem. Ind*, 1907, pp. 581-585) describes the carbonization of Durham coking-coal and the distribution of nitrogen and sulphur. The higher the temperature, the more ammonia is destroyed and the more cyanide is formed. He finds the liquor to contain 98·31 per cent. nitrogen as ammonia, 1·47 per cent. as cyanides, 0·22 per cent. as sulphocyanides. Of the sulphur, 90·46 per cent. is present as sulphide, 4·96 as sulphocyanide, 3·05 as sulphite and thiosulphate, 1·53 as sulphate.

Dunnachie (Fr P. 385066, 1907) withdraws the gases from coke-ovens, gas-producers, etc., from the hottest zone, where cyanogen and cyanides occur. These compounds are directly converted into ammonia by means of steam or atomized water, and if necessary, with a little air.

Lessing (Fr. P. 381186) prevents the gases and vapours, produced between the periods of coke-making, by an arrangement of valves, from entering the main receiver, where they might cause an explosion.

C. Otto & Co. (Ger. P. 203254) treat the hot coke-oven gases with a spray of tar or tarry gas-water, produced by a jet of air which at the same time aids in carrying away the gases. Coke-oven gas which before this treatment contained 45 g. of tar in a cubic metre, afterwards showed only 2·5 g., and can be introduced directly into the acid intended for absorbing the ammonia.

Hilgenstock (U.S. P. 1098900) removes the tar from the gases by treating them with a spray of tar, or of tar-water, and passing them into an acid-bath which gets heated by this proceeding, and retains the ammonia, allowing the other gases to go away.

Twynam (B. P. 1820, of 1914) converts the excess of coke-oven gases, not required for the working of the plant, first into mechanical energy, and then into electrical energy, which is utilized to produce nitric acid from the air; this nitric acid is used for absorbing the ammonia contained in the crude coke-oven gases to produce ammonium nitrate.

Bergfeld's Ger. Ps. 255593, 263905, and appl. B65600 also refer to this process.

Statistics on the Production of Ammonia from Coke-ovens.

The *Forty-fourth Report on Alkali, etc., Works* (for 1907), p. 46, gives the following statistics on the production of ammonia, etc., from coke-ovens, calculated as sulphate, in the United Kingdom. In 1886 the first Semet-Solvay recovery ovens were erected, in 1897 the first Otto-Hilgenstock ovens, and were followed by other types later on. The production in the year 1895 was under 2100 tons. The figures for recent years are:—

	Tons.		Tons.
1898	5,403	1903	17,438
1899	7,839	1904	20,848
1900	10,393	1905	30,732
1901	12,255	1906	43,677
1902	15,352	1907	53,572

In the United States, in the year 1914, 2,117,043 tons of coke were made; 67·2 per cent. of this in the old beehive ovens, and only 32·8 per cent. with recovery of the by-products.

In Germany the extension of this industry has been much faster. In the principal coke-producing district, that of Dortmund, the production of sulphate of ammonia from this source increased from 53,636 tons in 1903 to 155,191 tons in 1907.

AMMONIA FROM BLAST-FURNACE GASES.

The general principles of the recovery of ammonia, along with a certain description of tar, from blast-furnace gases have been mentioned in Chapter II., pp. 169 *et seq.*; and we must, in the first instance, refer to that description, more especially of the Gartsherrie process (Alexander and M'Cosh's). In this place we only mention those methods which, neglecting the tar, exclusively aim at recovering ammonia from blast-furnace gases.

To begin with, we point out that ammonia can be recovered only from such blast-furnaces as are worked with raw coal, since undoubtedly most of the ammonia comes from the nitrogen of the coal. But it is certain that some of it is formed from atmospheric nitrogen by reactions taking place within the furnace, principally those which in the first instance lead to the production of cyanides, which are thereupon decomposed by aqueous vapour, but only part of the ammonia thus formed is found in the gases escaping at the furnace mouth, much of it being decomposed again within the furnace.

Hilgenstock in 1885 pointed out that part of the ammonia found in blast-furnace gases should be attributed to the use of certain iron oxides containing water (brown hematites), especially such as have been kept a long time in contact with air.

In England the observation has been made (Hamilton, *Journ. West of Scotland Iron and Steel Institute*, No. 4, 1902; *Stahl u. Eisen*, 1902, p. 510) that sometimes coals, whose quality gives a right to expect a good yield of ammonia and which show such in the laboratory and at gas-works, give very little ammonia when employed in blast furnaces. The reason for this behaviour was sought in the large percentage of water in the ore, which somewhat reduces the temperature; but when this was reduced by partially or entirely roasting the ore, the yield of tar and ammonia did not rise, and the reason of this difference between the behaviour between English and Scotch coals has not yet been found.

Swindells and Lancaster (Fr. P. 115832, of 1876) believe they can recover, not merely the preformed ammonia, but also that obtainable by the decomposition of cyanogen compounds contained in blast-furnace gases, by means of superheated steam. The gases, after mixing with this, are passed through red-hot fuel, then through milk of lime, and finally through red-hot chambers filled with broken bricks, whereupon they are scrubbed for ammonia.

Chapman (B. P. 5523, 1881) passes the furnace-gases through a chamber in which there is arranged a set of perforated disks. The perforations, through which the gases are made to pass, are alternate, so that the perforation of one disk corresponds to a solid part of the next. The disks are fixed on a horizontal rotating shaft, and their lower parts dip in a vessel containing acid. The lid covering the disks also dips into the liquid, whose evaporating-water must be replaced from time to time. Another patent of the same inventor (B. P. 6406, 1884) contains some modifications of this process.

G. Neilson (B. P. 440, 1882) places a very large number of plates, made of earthenware or other material, so as not to be acted upon by acids, with interstices between them, in a chamber, and keeps them sprinkled with a dilute acid, while the gases are passed up between the plates; the ammonia salts formed drain off at the bottom.

John and James Addie (B. P. 4758, 1882) fix the ammonia in blast-furnace gases by mixing therewith sulphurous, or sulphuric, or hydrochloric acid in the form of gas or vapour, and subsequently condensing and recovering the ammoniacal salts formed. Their process has been discussed by A. Wilson (*J. Soc. Chem. Ind.*, 1883, p. 458). It was in the first instance devised in order to avoid the necessity of cooling the enormous amount of gases evolved from a blast-furnace, being thirteen times as much as that coming from a gas-retort for the same quantity of coal. The process has been successfully carried out at the Coatbridge works, and produces sulphate of ammonia of the finest quality. The method is based upon the treatment of the furnace-gases with sulphur dioxide, which is allowed to mix with them at any convenient part of the flue along which they pass. The result is the instantaneous formation of sulphite of ammonia, which is carried along by the current of gases. These are then washed in a perpendicular scrubber, the water being kept in circulation by a pump. When this system is applied to the treatment of producer-gas, whose temperature is much higher than that of blast-furnace gases, the scrubbers must be cooled from the outside by a shower of water. If the temperature of the gases does not exceed 260° C., all the water is used inside the scrubbers, and comes out as strong liquor. The specific gravity may be raised up to 40° or 50° Tw., if necessary, by the solution of salts of ammonia. This liquor is then converted into sulphate of ammonia by distillation in the ordinary way; but it may be employed for many purposes as it stands, without conversion into sulphate, such as, for instance, the production of ammonia for the ammonia-soda process or for the manufacture of liquor ammoniæ. The sulphite of ammonia thus obtained is always more or less mixed with sulphate and thiosulphate; but this, of course, is of no consequence, as the distillation with lime brings off the whole of the ammonia. Wilson gives the following analysis of the crude liquor of 15° Twaddell:—

	Per cent. weight in volume.		
Sulphate of ammonia . .	2·57	containing NH_3	0·66
Sulphite of ammonia . .	3·44	,, ,,	1·01
Thiosulphate of ammonia . .	4·18	,, ,,	0·96
Total ammonia-salts .	10·19	,, ,,	2·63

Another crude liquor, evaporated to dryness, gave a salt showing the following composition (Tatlock's analysis):—

Ammonium sulphate . .	36·13 per cent.
" sulphite . .	19·75 "
" thiosulphate .	33·10 "
Sodium sulphate . . .	8·58 "
Free sulphuric acid[1] . .	trace.
Insoluble	0·03 "
Organic matter . . .	2·11 "
	100·00[2]
Total ammonia . . .	20·31 per cent.
Equal to sulphate of ammonia	78·85 "

The sulphur dioxide used in this process is obtained from sulphurous shale, coal brasses, pyrites, etc., burnt in a retort by means of a forced current of air.

With regard to the question as to whether gas treated in this manner carries away any sulphur which might prove objectionable in metallurgical or other processes for which the gas is subsequently employed, it is interesting to quote the following testing (by Dr Clark) of Messrs Addie's gas-flue beyond the scrubbers, the apparatus being worked with excess of sulphur dioxide in the ordinary way:—

Sulphur per cubic foot of gas . .	10·1 g.
" per ton of coal burned . .	1·85 lb.
" per cent. of coal burned . .	0·08

Hence the sulphur in excess is only about one-tenth of the amount which must exist originally in the coal itself.

Instead of sulphur dioxide, R. Main and W. Galbraith (B. P. 10448, 1880) bring the gas from blast-furnaces, or that evolved in the destructive distillation of coal, shale, etc., into contact with a spray of hydrochloric acid, and afterwards convert the ammonium chloride into sulphate. This process (already suggested as far back as 1844 by Bunsen and Playfair) has never been carried out in practice, and Addie's process, also known as the Langloan process, *cf. supra*, p. 175, was only worked there from 1884 to 1892. In that year the Langloan furnaces were stopped, and when they were started again in 1900, the Dempster process was introduced.

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[1] How can free sulphuric acid exist in the presence of sulphite and thiosulphate?

[2] *Sic* in the original; the real total is 99·70.

J. Dempster (B. P. 11250, 1874) places between the blast-furnaces and steam-boilers or stoves where the furnace-gases are to be burned an ordinary ammonia-still, with its usual sulphate apparatus, "dust-boxes," and "condensers." The gases are then taken to washers and scrubbers, where the last traces of ammonia are absorbed.

Körting Brothers (*Dingl. polyt. J.*, ccliv., p. 260; *J. Soc. Chem. Ind.*, 1885, p. 220) have devised a special arrangement of pipes for cooling and washing the waste gas, as shown in Figs. 247 and 248. The tubes are arranged in three rows; and connections between the individual pipes of each row are so made that the gases pass up through one set of five pipes and down through the next. A set of 450 tubes, of 1 ft. diameter and 12 ft. long, gives a total surface of 18,300 superficial feet cooled by the air. An injector may be advantageously applied at different points of such a system.

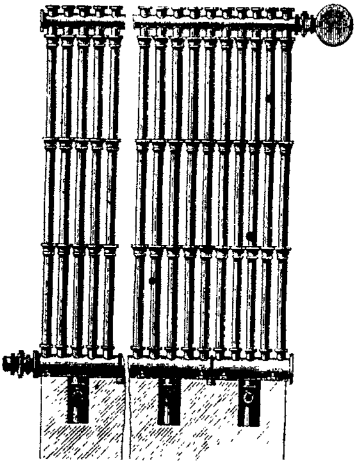

FIG. 247.

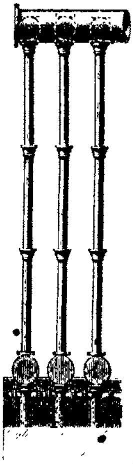

FIG. 248.

We shall also show here the washing-chambers, devised by Young and Beilby, intended to decrease the velocity of the stream of gas, and thus to effect a complete separation of tarry matters. In this arrangement (Fig. 249) the gases are introduced by the conduit *g*, and enter the chamber by the openings, *e e*, covered with leaden bells. A fine spray of water, or acid, is maintained during the passage of the gas. The washed gases pass away by *g*, the washings by *u*.

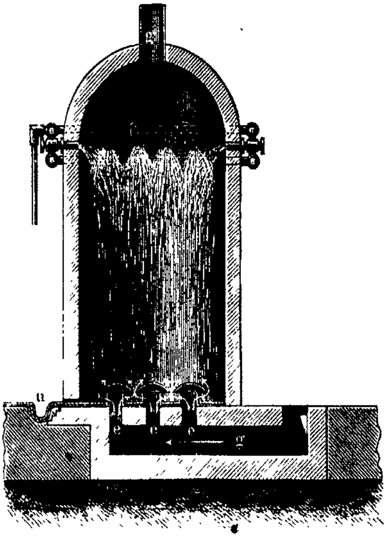

FIG. 249.

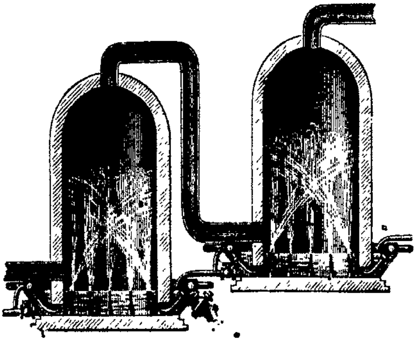

FIG. 250.

Fig. 250 shows a somewhat more advantageous arrangement, consisting of a series of chambers built on different levels, so that the liquid employed for washing can be introduced at the opposite end of the system to that at which the gas enters, and passes simply by gravity through the whole series, until spent. Thus it is not necessary to lift the liquid to the top of the chamber and there to spray it. The size of the chambers is such that for 100 cub. ft. of gas passed through in twenty-four hours, at least 0·5 cub. ft. of space is provided. Large chambers, in which the cooled gases can come to rest and deposit their particles of tar, appear to be most suitable for the complete separation of the tar.

Mackay (B. P. 14060, 1889) scrubs the gases successively with water and tar-oil, to extract all the ammonia and tar. He first cools them by passing them in annular jackets round the absorbers. Other patents for the purpose in question have been taken out by Imray (B. P. 19589, 1894) and the Coltness Iron Co. (17673, 1899).

At the Summerlee iron-works the gases formerly were, without previous cooling, brought into contact with sulphuric acid in lead-lined towers, thus obtaining a solution of ammonium sulphate. That process was a precursor of the Mond process (p. 1213), but it was abandoned in 1901 and arrangements were made to cool and wash the gases with water, as it is done at all other Scotch iron-works.

R. Hamilton described a process for producing ammonium carbonate from blast-furnace gases, which certainly contain all the CO_2 and H_2O required, but the product never came out sufficiently pure.

Reininger (Ger. P. 167033) increases the yield of ammonia in blast-furnace work by introducing an alkaline carbide into that part of the furnace where the temperature is about 800° to 1000° C.

The recovery of the by-products from the gases of Scotch blast-furnaces is discussed in detail in the *Transactions of the Institution of Engineers and Shipbuilders in Scotland*, 1896, part 25 (*Stahl u. Eisen*, 1896, p. 383). The quantities of ammonium sulphate recoverable from this source (which must be approximately the same as in the gas from Carvès coke-ovens, *i.e.*, 0·9 to 1·36 per cent. of the coal) are quite considerable. Assuming a yield of 11·3 kg. of sulphate of ammonia per ton of coal, and the yearly average coal consumption of the Scotch blast-furnaces = 2½ million tons, the production of sulphate of ammonium from this source would be 28,250 tons per annum. This calculation cannot be applied to the English and Welsh blast-furnaces, because these work with coke, while the Scotch furnaces are worked with splint coal.

According to the *Forty-fourth Report on Alkali, etc., Works* (for 1907), p. 45, iron-works recovering ammonia from blast-furnace gases are almost entirely confined to Scotland, since only in special districts coal is found of sufficient hardness to stand in the blast-furnace without crushing. The English works of this class are confined to Staffordshire.

AMMONIA FROM PRODUCER-GAS.[1]

We have had occasion before to mention the recovery of ammonia from the aqueous fluid condensed from gas-producers or "generators"; thus in connection with the processes of Mond and of Addie (pp. 1213 and 1246), which Wilson believes to be applicable to his gas-producers. Evidently most of the processes described in the preceding and in the following sections would apply to gas-producers, provided the ammonia recovered paid for the cost of the operation, and that the latter did not injure too much the efficiency of the gaseous fuel, which in any case it will do by cooling it.

We may also mention the process of Fogarty (p. 1119), although in this the ammonia originally present in producer-gas plays only an insignificant part.

Rigby (B. P. 20716, of 1901) describes a condensing-apparatus for that purpose.

According to the B. P. 18558, 1914, of Rigby and Wet-carbonizing Ltd., peat which has been treated by heat, or wet-carbonized, is used as absorbent for ammonia from gas-producers. The ammonia fixed by the peat is not liberated below 100°, and the product possesses valuable fertilizing power; its nitrogen content can be raised to about 3 per cent.

In ordinary cases it does not pay to take the ammonia out of producer-gas, as this contains much less of it than coke-oven gas, and the expense of cooling and washing for a certain yield of ammonia is too great, or even quite prohibitive when anthracite or coke is used, as is altogether the rule for gas-producers. There is no getting over the fact that the temperature at which the producers must be worked to yield a good quantity and quality of gas, say from at least 800° up to 1000° C., is deleterious to ammonia, the decomposition of which, when not protected, according to Ramsay and Young, begins at 500° and is fairly complete at 780° C. The presence of a large volume of steam or of hydrogen, etc., retards the decomposition of the ammonia; but in ordinary cases, anyhow, not much of it is found in producer-gas (*cf.* Rowan, *Iron and Steel Trades Review*, 1908, p. 1594).

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[1] *See* also *supra*, pp. 1207 and 1231.

The case is, of course, different when the recovery of ammonia is purposely made a principal feature; this case has been already treated on pp. 1207 *et seq.*, especially the Mond process.

Woltereck (*cf. supra*, p. 1231), in *Comptes rend.*, 1907, p. 929, discusses the formation of ammonia and cyanides in a Dowson gas-producer.

Lymn (B. P. 8014, of 1908) describes an absorbing-apparatus for the ammonia in producer-gas.

Jacob Wolf (Ger. P. 281317) obtains ammonia from a mixture of carbon monoxide, nitrogen, and water, by adding the water only after the mixture of carbon monoxide and nitrogen has left the producer-space. According to him, the yield of ammonia from the usual gas-producers could not be satisfactory, since the temperature in these is much too high for the stability of ammonia, nor can the temperature in the producers be lowered, or the heat be fully utilized—drawbacks which are avoided in his process.

Koppers (Ger. P. 279550) increases the rate of working and the production of ammonia in gas-producers by introducing a combustible gas such as hydrogen, keeping the temperature high enough to burn it.

The production of tar and ammonia from water-gas is described in the B. P. 2650, of 1914, of Moore, Dowson, and Mason's Gas Plant Co.

Besemfelder (*Chem. Zeit.*, 1915, p. 925) recommends, in lieu of burning coal in the usual way for household and industrial purposes, to convert it into "mixed gas" of constant composition, whereby not merely tar and benzol are obtained, but the yield of ammonia is raised from 14 to 70 per cent. of the nitrogen of the coal.

Sachs (B. P. 28735, 1913; Ger. P. 274011) withdraws the gas from the interior of the fuel through perforated tubes, provided with a cooling-device (such as a coil or water-jacket), whereby up to 90 per cent. of the nitrogen of the fuel can be obtained as ammonia.

AMMONIA FROM ORDINARY PRODUCTS OF COMBUSTION (COAL-SMOKE).

We comprise in this section the attempts at recovering ammonia from other sources than those previously enumerated; especially from the products of combustion in ordinary cases, or where they are mixed with vapours more charged with ammonia, *e.g.*, when carbonizing bones in pot-furnaces. In these cases the methods hitherto enumerated are not sufficient to sift out, as it were, the very small quantity of ammonia from among an enormous volume of diluent gases; nor can it be said that this problem has been satisfactorily solved by any inventor.

Fr. Lorenz (B. P. 6008, of 1882; Ger. Ps. 26638 and 26979) employs the gases from bone-char furnaces first for raising steam, and then passes them through regenerators, to give up most of their heat. After this they are mixed with hot steam; the mixture of gases and steam is sent into a scrubber; the cold gases coming from the scrubber are first reheated, in order to again saturate them with steam, by being made to traverse the regenerators in a direction opposite to that of the gases coming direct from the furnaces, and are then sent into another scrubber fed with dilute sulphuric acid. [The idea of mixing the furnace-gases, containing an exceedingly minute quantity of ammonia, with steam, or water in a fine spray, vaporized by the heat of the gases, in order to make the ammonia more easily condensable in a scrubber, because only in this way would there be a sufficient contact with water for all the dispersed molecules of ammonia, was suggested to the "inventor" in a detailed memoir sent to him by myself (Lunge) on 29th June 1881. This idea has been incorporated in the above patent, without leave being given or any notice received by me.]

H. Neumeyer (Ger. P. 24511) employs hot sulphuric acid for absorbing ammonia from gaseous mixtures. The acid is converted into a fine spray, by issuing under pressure from holes in a vertical pipe, made of an alloy of lead and antimony, and strikes against the sides of an outer pipe, while the gases containing ammonia travel through the annular space between the pipes. The liquor collecting at the bottom is heated by a steam-coil, and by a force-pump is pumped back into the spray-producer. Thus a hot and concentrated solution is obtained, from which ammonium sulphate separates on cooling.

H. Wellstein (Ger. P. 28762) likewise employs a spray of heated sulphuric acid, which strikes against the cover of the chamber through which the gases containing ammonia are made to travel; whenever a certain quantity of liquor has collected at the bottom of the chamber, it passes through an automatically opening valve into a pulsometer, where it is subjected to heating from without, and the vapour generated thereby causes the pulsometer to act, and to force the acid liquor back again into the upper reservoir, till it is completely saturated with ammonia.

The Société anonyme Lorraine industrielle de Hussigny (B. P. 5828, 1884) recommends the absorption of ammonia from furnace-gases by calcium chloride. The mixture of calcium carbonate and ammonium chloride formed is either to be used as an ammoniacal manure, or, by heating, sesquicarbonate of ammonia can be obtained, which is to be employed in the ammonia-soda process.

Dow (U.S. P. 733465) also brings the gases into contact with a hot solution of calcium chloride, adds calcium hydroxide, and blows out the ammonia by a relatively cool gas.

W. Forster (*Chem. Zeit.*, 1894-1895) found in the soot from a coal-fire 11·55 per cent. ammonium sulphate. [This seems to be quite an exorbitantly high figure, which cannot be accepted as valid for ordinary purposes.]

CHAPTER XII

HISTORICAL NOTES ON AMMONIA

RISE AND FUTURE OF THE INDUSTRY OF AMMONIA.

Historical Notes on Ammonia and its Compounds.[1]

THE knowledge of *free* ammonia cannot be pursued further back than the seventeenth century. But long before that time certain compounds of ammonia have been utilized for various purposes, of course without any idea of their essence. We begin with that which is the earliest known—*Sal-ammoniac* (Ammonium chloride).

Dioscorides, in his *Materia Medica*, written about the year 50 after Christ, makes some remarks on the fumigation with hartshorn, on the properties of putrefying urine, and on the nauseous smell of crude "nitron" (impure soda) and some descriptions of alum. Pliny (Kopp, *Gesch. d. Chem.*, iii., p. 236) also mentions the smell of the "nitron," principally coming from Egypt, given off on contact with lime "Calce aspersum reddit odorem vehementum." This might lead to the conclusion that the Egyptians already in the commencement of our era were acquainted with the preparation of *ammonium carbonate*, which they confounded with "nitrum," the saltpetre of the ancients, because its effects in some respects are the same. At all events the ancients knew that putrefied urine is of alkaline nature (as we express it now), and utilized this by employing it for washing purposes, like alkaline dyes.

It is true that much earlier, in the fifth century before Christ,

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[1] We follow here in many points the paper by E. O. von Lippmann, in *Chem. Zeit.*, 1909, No. 14; otherwise the treatment of this subject in Lunge and Koehler's *Steinkohlenteer und Ammoniak*.

Herodotus speaks of the "hals ammoniakos," *i.e.*, ammoniacal salt; but he evidently meant the crystallized rock-salt (sodium chloride) found in the Oasis of Jupiter Ammon, and so do all the following Greek and the later Syrian and Arabian authors, up to the sixth century of our era. This is unmistakably proved by the writings of other Greek and Latin authors, quoted by Kopp, *loc. cit.*

The question at what time "Ammonia" in the present meaning has been first mentioned, is complicated by the fact that the word "ammonia" occurs in two entirely different meanings. With one of these, the "gum ammoniac" (which is a kind of resin obtained from an umbelliferous plant growing in abundance near the temple of Jupiter Ammon, in Egypt), we have nothing to do here. The other meaning of "ammoniakon," or "sal ammoniacum," is that which we now connect with the word "sal-ammoniac," *i.e.*, ammonium chloride. The word ammoniakon occurs in the first meaning already in the writings ascribed to Hippocrates, and dating from the fifth century before Christ; also in those of Pliny, Dioscorides, and other authors of the classical times, as well as later on in the writings of mediæval Arabians and Europeans.

According to Treumann (*Chem. Zeit.*, 1909, p. 49) and Schöne (*ibid.*, p 77) the "Armoniacum," mentioned in the Hortus Sanitatis of 1555, means the gum-resin just mentioned. According to Lippmann (*ibid.*, pp. 117 and 186) that word in the Hortus Sanitatis means both the gum-resin and the ammonium chloride, which was already known by Pliny, who rather indistinctly speaks of it as sometimes occurring in Egyptian "nitron" (natural soda). But a more accurate knowledge of it dates only from the development of the processes of sublimation and distillation in Egypt, about the fourth century after Christ, since it was evidently observed when burning camel dung in fireplaces provided with a chimney. The Arabian polyhistor, Al-Garitz (deceased in 869 A.D.), mentions sal-ammoniac as one of the matters well known to have been obtained by the Arabs from the Greek, by the Persian name "nashadir" or almizadir," which is found in various other Arabian and Persian authors later on (who by the word "ammonish salt" always understood rock-salt, *vide supra*). As "sal armoniacum," pure sal-ammoniac is first mentioned by the European chemists of the twelfth century, and frequently in the sixteenth and seventeenth centuries, either in that form or in that of "sal ammoniacum."

According to Schramm (*Chem. Zeit.*, 1909, p. 529), the first occurrence of the words "sal armoniacum" in the meaning of ammonium chloride in print is in a booklet on the removal of grease spots, printed in 1532 by Peter Jordan, at Mayence. The word "salmiak" occurs first about 1700.

The first reliable communications on real sal-ammoniac (ammonium chloride) are found in a treatise of Geber (who lived from 701 to 765 of our era), with the title *De investigatione magisterii*, in which he accurately describes its preparation and sublimation from urine and salt. In the subsequent translations of that book that salt is quoted as "sal ammoniacum" or "armanoriacum." Basilius Valentinus (in the fifteenth century) cites it as "salarmoniac," "armenisches Salz," "Salz aus Armenia," or "armenischer salarmoniac." According to Kopp (*loc. cit.*) it cannot be assumed that sal-ammoniac has been brought to Europe before the seventh century after Christ; it probably came from the Central-Asian volcanoes under the designation of "Armenian salt," which in the course of time changed into the words sal armoniacum, sal ammoniacum, and salmiak (the present German designation). It is also well known that sal-ammoniac during a long time was imported into Europe from Asia, and especially from Egypt, where Sicard (1716), Léméry (1719), and Duhamel (1736) saw its preparation from camels' dung.

Much later, in the second half of the seventeenth century, the preparation of sal-ammoniac on a large scale commenced to be practised in Europe. Here also at first the material to start from was the urine of men or animals. According to Kopp, the first factories for the production of sal-ammoniac were those of Dovin and Hutton, at Edinburgh (1756), Gebrüder Gravenhorst, at Brunswick (1759), and Baumé, in Paris (about 1770). We must look at sal-ammoniac as the first product of the industry of ammonia which has been obtained on a large scale with a clear aim. Subsequently it has served as starting-material for the preparation of all other salts of ammonia, and for that of free ammonia itself.

Of much later date is the recognition of *Ammonium Carbonate* and that of *Free Ammonia.* Kopp, who made a painstaking search in the Arabian writings coming into question, and especially in those of Geber, could not find any positive statements on them; nor is this the case with the places in Dioscorides and Pliny. The first distinct mention is found in the *Experimenta* of Raymundus Lullus, written in the thirteenth century, who describes the preparation of the "volatile alkali salt" from putrefied urine, and draws attention to its great volatility, and its strong smell. In the fifteenth century Basilius Valentinus showed how that salt, which he calls "spiritus salis urinæ," can be obtained in a simpler way by distilling sal-ammoniac with Oleum tartari (potassium carbonate). His idea of the formation of "spiritus urinæ" in the human organism is exceedingly naïve. According to him that salt is formed in the human body from wine, which makes its way into the urine, where the salt is then found. Since in Armenia the best wine is drunk, and the men's urine serves for preparing the salt of Armenia "so nimmt es nicht so langes Wesen, den Spiritus salis urinæ daraus herzustellen." But the preparation of ammonium carbonate during a long time after that took place principally from blood, bones, hartshorn (therefore the designation "Hirschhornsalz"), ivory, and other animal matters. As late as 1713 Biet prescribes its preparation by distilling 5 lb. of the skull of a man, died on the gallows, or in some other unnatural way, with 2 lb. of dried vipers, hartshorn, and ivory.

No doubt Basilius Valentinus, who distilled sal-ammoniac with lime, and Robert Boyle, who employed lime for preparing "volatile alkali salt" from animal matters, must have had *free (caustic) ammonia* in their hands; but they did not recognize it as different from "volatile alkali salt"; no more did Lémery (1865), who distilled sal-ammoniac both with lime and with potashes, but did not recognize any difference between the products of these two operations. Van Helmont, the most celebrated naturalist of that epoch, considered the solidification of volatile alkali salt by spirit of wine to be the cause for the occurrence of urinary calculus in the human body.

The first certain indication of caustic ammonia is made by Kunkel (1716), who compares it with the caustic alkalis, and points at its difference against the mild (carbonated) alkalis.

The designation of "spiritus volatilis salis armoniacum," introduced by Glauber already in 1658 for the volatile alkali salt, was now changed into "alcali volatile salis ammoniacum," and abbreviated in 1782 by Bergman and the French chemists of that time into "Ammoniacum," "Ammoniaque," "Ammoniak."

The discovery of *gaseous ammonia* dates only from 1774, when Priestley distilled sal-ammoniac with dry caustic lime, and collected the gas given off over mercury. He very soon recognised its alkaline quality, and called it "alkaline air." Basing on this discovery, and on the previous work of Priestley and Scheele, Berthollet, in 1785, and still more distinctly in 1805, finally established the composition of ammonia $= NH_3$, by decomposing it by means of the electric spark.

Of other compounds of ammonia, known to the chemists of former times, we mention the *sulphate*, described by Libavius in 1595 in his *Alchymia;* later on Glauber prepared it by saturating sulphuric acid with volatile alkali, and called it "sal ammoniacum secretum Glauberi." He also prepared the *nitrate* by saturation of nitric acid, and described it as "nitrum flammans." Compounds of ammonia with *sulphur* were prepared already in the fifteenth century by Basilius Valentinus, by distilling sal-ammoniac with lime and sulphur, or of "spiessglas" (antimonium sulphide), lime, sal-ammoniac, and sulphur. Later on ammonium sulphide was described by Beguin (1608) and Boyle (1663), after whom it was frequently designated as "Spiritus fumans Boylei."

The *application* of ammonia and its compounds in former centuries was confined to medical purposes and purely scientific investigations; only that of sal-ammoniac for the tin-coating of metals is mentioned by Agricola (1490 to 1555). Up to the end of the eighteenth century there is no trace of an *industrial production* of ammonia and its salts. Even towards the middle of the last century one of the most distinguished chemists of that time, J. Dumas, mentions the ammonia salts only as "rather important" for technical purposes, and probably more so at no distant time. Their consumption, he says, would be considerably increased if they were introduced into agriculture for manurial purposes, on which point experiments were going on in several countries. As raw materials for a profitable production of ammonia Dumas mentions animal substances, such as the carcases of various animals, camels' urine and fæces, urine from privies, and the ammoniacal liquor of gas-works, as well as the residue from purifying gas by solutions of metals, but principally bones, which on destructive distillation furnish an ammoniacal liquid. He goes into some details on the recovery of ammonia in the shape of sulphate by filtering gas-liquor, or the richer liquor obtained by the charring of bones over gypsum, or by distilling this, or putrefied urine, with lime in vessels provided with agitating-apparatus, collecting the vapours in sulphuric acid of 52° Bé., and boiling down the solution of sulphate of ammonia up to the crystallizing-point.

As late as 1869, R. Wagner (*Chemische Fabrikindustrie*, 2nd ed., p. 401) mentions urine and the products of the charring of animal substances as important sources of ammonia; but already in 1873 (*Chem. Technologie*, 9th ed., p. 273) he says that these sources of ammonia have lost their importance since the general introduction of the illuminating-gas made from coal, and the working of the gas liquor obtained in this for ammonia salts.

But even at that time the ammoniacal liquor, as well as the tar obtained as by-products in the coal-gas manufacture, were considered as troublesome matters. In 1863 d'Hurcourt (*Eclairage au gaz*, p. 208) states that the Compagnie Parisienne du Gaz, which had commenced to work up its own gas liquor for ammonia salts, made such small profits therefrom that it hardly paid the costs. Moreover, the public authorities interfered very much with this industry on account of the nuisance caused by bad smells. Schilling states in 1869 (*J. Gasbeleucht.*, p. 355) that the gas-works had to spend a good deal of money to get rid of the gas-liquor; and in 1874 (*ibid.*, 1874, p. 118) one of the most important German gas-works was compelled to carry their large production of gas liquor in tank-carts through the town, in order to run it into the river below it.

Since then the state of matters has very much changed. It has become more and more certain, in the first instance through the labours of Liebig and his school, that there is a vast field for the application of nitrogen compounds for agricultural purposes. It is true that for a considerable time the requirements of the soil for nitrogen had been satisfied by means of the nitrate of soda, found in Chili. In fact most cultivated plants assimilate the nitrogen offered to them only in the form of nitrates, and the ammonia must be transformed by the action of microbes into nitrates, before the plants can benefit from it. Consequently its action is slower than that of the nitrate, but all the more lasting, since it is also in the shape of sulphate absorbed by the soil and retained in it, whereas the nitrate of soda is liable to be washed out of the soil by rain and other forms of humidity. It has taken considerable struggles to attain for sulphate of ammonia a rank equal to that of nitrate of soda in the tilling of the soil; but nowadays agriculture is by far the greatest consumer of ammonia, in sharpest competition with nitrates, as predicted by Dumas half a century ago.

But also for industrial purposes the application of ammonia has made immense strides since that time. We will mention only a few proofs of that. In the manufacture of alkali, the ammoniacal soda process, in the first instance through the work of Solvay, has got entirely the upper hand over the old Leblanc process. Large quantities of ammonia are absorbed by the industry of coal-tar colours, by bleachers, dyers, and calico printers; smaller, but very sensible quantities for the zinc-coating (galvanizing) of iron, and in the galvanic industry altogether. Quite a new application of ammonia is that for producing low temperatures, which acted back on itself, by the successful introduction of the liquefying of ammonia on a large scale. Such compressed, liquefied ammonia is now manufactured on an immense scale, and serves not merely for the production of cold (by Linde's and other ice-machines), but owing to its easy manipulation and carriage it has replaced ammoniacal liquor in many cases in chemical industries. The industry of explosive matter, and quite recently that of artificial silk, also absorb considerable quantities of ammonia.

Owing to the increased demand for ammonia and its salts, *the gas-liquor*, formerly such a source of trouble, has become a valuable by-product, just like its companion, coal-tar, and nowadays is an important factor of the rentability of gas-works; also of that of coke-works, in Germany certainly much more so than in Great Britain. In course of time a great many proposals have been made for transforming a larger proportion of the nitrogen of coal into ammonia, as we shall see. At larger gas-works the liquor is worked up on the spot for sulphate of ammonia or concentrated ammoniacal liquor; this goes to the ammonia factories, which also get the ordinary gas liquor direct from the smaller gas-works.

The recovery of ammonia at *gas-works* has in the course of time reached very large dimensions, but during the last ten or twelve years it has, at least in Germany, been far outdone by the production of ammonia in *by-product coke-ovens.* The question may now be raised, what is the outlook for the future as to the development of this industry? According to Rau (*Stahl u. Eisen*, 1910, p. 1290) the production of ammonium sulphate during the first decade of this century has risen from 104,000 to 323,000 tons, the consumption from 125,000 to 322,000 tons, that is almost by 300 per cent., whilst the total consumption of nitrate of soda in the same space of time had risen from 470,000 to 637,000 tons—that is merely by 36 per cent.; the share of ammonia in the supply of nitrogen altogether had risen from 26 to 40 per cent., for agricultural purposes from 31 to 47 per cent. Great competition for supplying nitrogen to the soil is now made by the *fixation of atmospheric nitrogen.* The manufacture of calcium nitrate by one of these processes alone, that of Birkeland and Eyde, was to be 100,000 tons in 1912; that of cyanamide ("lime-nitrogen"), by the process of Frank and Caro, was to be 100,000 tons in 1912, and the total quantity of "lime-nitrogen" = 233,000 tons. Besides this, the synthesis of ammonia from atmospheric nitrogen by the process of Haber and others, which we shall describe later on, is making more and more progress.

Even the aid of microbes has been invoked for fixing atmospheric nitrogen and working it up into vegetable substances. Pure cultures of such nitrogen-assimilating bacteria are sold by the Farbwerke Höchst under the name of "Nitragin," and by the Farbenfabriken Elberfeld as "Alinite." But up to the present no tangible results on a large scale have been attained in that quarter.

Another point is of the greatest importance for the future of the ammonia industry, viz., the unavoidable exhaustion of the Chilian beds of nitrate of soda within a few decades. In 1904 it was calculated by Semper that these beds, at the then existing rate of consumption, would last another forty-four years; and since that time the consumption has increased by about one-third.

In conclusion, we may venture to take the following views concerning the *future* of the ammonia industry. In the course of years the supplies of nitrate from Chili must diminish and ultimately cease; all the greater will be the demand upon ammonia products for agricultural purposes; nay, even the conversion of ammonia into nitric acid, by the process of Ostwald or in other ways, will increase the demand for ammonia. The synthetical production of ammonia from atmospheric nitrogen must find its limits in the impossibility of producing the requisite enormous amount of electrical energy *in infinitum*, whether by water-power or otherwise. As far as we can look forward, the principal source of ammonia will be always the nitrogen of coal, just as this has been the case for a long time past in the case of the comparatively small fraction of coal consumed for the manufacture of illuminating-gas, and more recently by carrying out the coking of the coal in such a way that the formerly lost by-products, ammonia and tar, are recovered. This last proceeding is sure to be more and more extended. Even the general conversion of the coal to be used for heating, into gaseous fuel, with recovery of its nitrogen in the shape of ammonia, is within visible distance.

CHAPTER XIII

SOURCES FROM WHICH AMMONIA IS OBTAINED

NATURAL OCCURRENCE OF AMMONIA.

AMMONIA, especially as carbonate, is found almost everywhere in soil, water, and air, as a product of the decomposition of organic bodies, but in very slight traces. Although the growth of plants seems altogether to depend upon the ammonia thus presented to them and upon the nitrates formed by the oxidation of that ammonia (along with that formed by the electric discharge), yet this ammonia is diluted to such an enormous extent that it will ever be out of the question to recover it in substance.

In some cases rather more ammonia is collected in one spot, owing to the absorptive faculty of some kinds of clay, of peat, etc. But even in such cases it would seem hopeless to recover it in a direct way, although this sometimes becomes possible indirectly, when the materials in question are subjected to processes for recovering other useful substances, *e.g.*, peat to dry distillation, for the purpose of extracting oils and paraffin. Indeed, the principal source of ammonia, coal, seems to owe its nitrogen in a great measure to the absorptive faculty of some forms of decaying organic matter for the ammonia of air, and of that produced within its own mass.

A more direct opportunity of recovering ammonia is presented when, under favourable circumstances, the ammonium salts formed in the decomposition of organic matter are not, as usual, at once diluted and dispersed, but are allowed to collect and concentrate. Thus solid ammonium carbonate is found in the *guano deposits* on the west coast of South America, sometimes in such large quantities that it can be exported to Europe. Such ammonium salt first appeared in